Growth and Characterisation of InP Nanowires and Nanowire-Based Heterostructures for Future Optoelectronic Device Applications

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The Australian National University
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.

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Abstract

Indium Phosphide (InP) forms a cornerstone amongst direct band-gap III-V compound semiconductors with the possibility for a wide range of other III-V alloys to be lattice matched with it. It is commonly used in optical communications related device applications, high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs). The very low surface recombination velocity of InP has made its nanowire counterpart a standout amongst nanowires of other III-V materials with successful demonstrations in nanowire solar cells, lasers and single photon sources. Considerable progress has been made in terms of InP nanowire growth in the past decade. Defect-free wurtzite (WZ) phase nanowires with good optical quality have been achieved on InP (111)B substrates. However, there are unexplored areas related to nanowire heterostructures that may hold promise for future device applications. Furthermore, InP nanowires aimed for future integrated devices need to be grown on the Si (111) substrates, and preferably on Si (100) substrates, in order to be integrated with microelectronics and other planar devices on a single chip.

This dissertation presents a progressive advancement of Au seeded InP nanowire growth by MOVPE, from heterostructures grown on InP (111)B substrates to nanowire growth on Si (111) substrates and [100] oriented InP substrates. A number of diverse techniques have been employed to understand the growth process and characterise the samples. 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 room and low temperature photoluminescence (PL) and PL mapping have been used for optical characterisation.

InP-In$_{x}$Ga$_{1-x}$As nanowire quantum wells (QWs) emitting in the 1.3 μm optical communications wavelength region are grown on InP (111)B substrates. Detailed structural and optical analysis carried out using cross-sectional TEM (X-TEM) and PL mapping reveal asymmetric diffusion at the two interfaces of the QW, and broad, yet bright and homogenous PL emission along the complete length of the nanowire, with no emission visible from the InP nanowire core or outer barrier. The emission wavelength of the QW is tuned in the 1.3 μm range by varying the QW thickness as well as composition. The WZ phase QWs are optically modelled using the k-p method. Multiple QWs comprised of three QWs and showing strong emission is also demonstrated.
Abstract

InP nanowire growth on Si (111) substrates has been carried out using an intermediate buffer layer. A two-step approach is used for the growth of the buffer layer and the growth parameters are optimised for both steps in order to achieve a smooth layer that covers the underlying Si substrate. It is seen that the layer fully relaxes by forming dislocations at the interface and is of (111)B polarity. Over 97% vertical nanowire yield is achieved on the buffer layers, and these nanowires are found to be similar in morphology and optical properties to those grown homoepitaxially on InP (111)B substrates under the same growth conditions.

InP nanowires grown on the industry standard [100] orientated substrates are examined by studying the growth directions, facets and crystal structure of the different types, namely, vertical, non-vertical and planar nanowires grown on InP (100) substrates. The seemingly random growth directions of the non-vertical nanowires are actually found to be <111> and <100> directions that acquire complex orientations with respect to the substrate due to the consecutive three dimensional twinning that takes place at the initial stages of growth. These directions are mathematically calculated and verified by the measurements carried out on individual nanowires. It is shown that 99% of the nanowires grown on InP (100) substrate are either <100>, <111> or <110> oriented with growth facets of either {100} or {111}.

The relative yields of each type of nanowire grown on InP (100) substrates are controlled by optimising the pre-growth annealing and growth conditions. A maximum of 87%, 100% and 67% yield is achieved for vertical, planar and non-vertical nanowires, respectively. The novel families of side facets of <100> nanowires are engineered to obtain cross-sectional shapes ranging from square to octagonal while maintaining a high vertical yield. Growth parameters and post-growth in-situ annealing conditions are tuned in order to achieve this. Finally, InGaAs QWs are grown on a novel and asymmetric facet combination of [100] nanowires, demonstrating the intended non-uniform complex growth that results in different thicknesses and compositions on the different types of nanowire facets.

Overall, this work explores new avenues of InP nanowire and heterostructure growth aimed for future optoelectronic devices that are directly integrable with planar devices and Si technology. The findings presented, especially those on growth on [100] oriented substrates, bring many unforeseen opportunities for nanowire device development to light.
Publications

Journal Articles


Conference Papers


## Acronyms and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>a.u</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>As</td>
<td>arsenic</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>arsine</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>Avg</td>
<td>average</td>
</tr>
<tr>
<td>BSE</td>
<td>back scattered electrons</td>
</tr>
<tr>
<td>DI</td>
<td>deionised</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>Ga</td>
<td>gallium</td>
</tr>
<tr>
<td>HAADF</td>
<td>high angle annular dark field</td>
</tr>
<tr>
<td>In</td>
<td>indium</td>
</tr>
<tr>
<td>MOVPE</td>
<td>metal organic vapour phase epitaxy</td>
</tr>
<tr>
<td>MQW</td>
<td>multiple quantum well</td>
</tr>
<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>NW</td>
<td>nanowire</td>
</tr>
<tr>
<td>P</td>
<td>phosphorous</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>phosphine</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dot</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<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>RMS</td>
<td>root mean square</td>
</tr>
<tr>
<td>RSM</td>
<td>reciprocal space map</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SADP</td>
<td>selected area diffraction pattern</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SF</td>
<td>stacking fault</td>
</tr>
<tr>
<td>Si</td>
<td>silicon</td>
</tr>
<tr>
<td>SQW</td>
<td>single quantum well</td>
</tr>
<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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<tr>
<td>VLS</td>
<td>vapour-liquid-solid</td>
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<tr>
<td>VS</td>
<td>vapour-solid</td>
</tr>
<tr>
<td>WZ</td>
<td>wurtzite</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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<tr>
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<td>cross-section TEM</td>
</tr>
<tr>
<td>ZB</td>
<td>zincblende</td>
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Chapter 1

Introduction

1.1 InP Semiconducting Material

InP is a commonly used III-V compound semiconductor that has a direct band-gap. The two common group IV elemental semiconductors, Si and Ge, have indirect band-gaps. This leads to lower radiative recombination efficiencies. Therefore, direct band-gap is one of the main advantages of most III-V compound semiconductors that are formed by combining elements from the groups on the either sides of the group IV in the periodic table. Band structures of semiconductors will be discussed further in Chapter 2.6 and 2.7.

However, the key property of InP, which makes it a stand-out amongst other direct band-gap III-V compound semiconductors is its lattice parameter. As seen in Figure 1.1, InP can be lattice matched with a wide range of other ternary and quaternary semiconducting materials that have a range of band-gaps and band alignment types with InP (note that only some key possible combinations are shown in Figure 1.1 for clarity). For example, lattice matched InAlAs has a higher band-gap than InP, while InGaAs has a lower band-gap [1]. This gives enormous freedom in designing InP-based heterostructures. While most materials show type I band alignment with InP, materials such as lattice matched GaAsSb shows type II band alignment with InP [2, 3]. The possibility to lattice match with InGaAsP and InGaAs, that can be tuned to emit in the 1.3 and 1.55 μm optical communication wavelength regions makes InP indispensable in photonic devices such as photodetectors, laser diodes, modulators, light emitting diodes and waveguides that are used in communication systems [4-14]. Optical communication related applications in fact, are the most popular type of thin film-based application that uses InP [15].

Lattice matched InGaAs layers sandwiched between InP have high carrier concentrations and electron mobilities [16]. They facilitate high frequency applications such as high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs), and have demonstrated speeds exceeding 40 Gb/s and record breaking frequencies in the 1 terahertz range [12, 17-19]. The mobilities achieved in InP-based structures are far superior to those achieved in the other popular lattice matched material combination, which is GaAs-AlGaAs [16, 20].
Introduction

Figure 1.1: Band-gap/wavelength against the lattice parameter of some common semiconducting materials, adapted from [21]. The region shaded in grey indicates the lattice parameter range within ±1% of InP.

The value of the band-gap of InP, which is 1.35 eV at 300 K, is also advantageous for many applications. Solar cell is one of these and the band-gap in this region ensures high energy conversion efficiency [15]. Solar cells have been fabricated by combining other lattice matched materials as well as by only using InP doped layers [22-25]. High resistivity against radiation makes InP solar cells the best suited for space satellites [23, 26, 27]. The relatively high optical absorption coefficient also contributes to the success of InP solar cells [28, 29]. In the recent years, InP solar cells have been more successful in nanowire form [29-33]. This will be discussed in detail in the following section. In addition, lower surface recombination velocity which enhances minority carrier lifetimes and higher thermal conductivity which helps in power dissipation in electronic devices make InP a much favoured semiconductor [16, 34, 35].

Table 1.1 gives reported values of some of the above discussed material parameters (at 300 K), for InP, compared with other common semiconductors.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si</th>
<th>InP</th>
<th>GaAs</th>
<th>InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter (Å)</td>
<td>5.431</td>
<td>5.8687</td>
<td>5.65325</td>
<td>6.0583</td>
</tr>
<tr>
<td>Band-gap (eV)</td>
<td>1.12 (indirect)</td>
<td>1.344 (direct)</td>
<td>1.424 (direct)</td>
<td>0.354 (direct)</td>
</tr>
<tr>
<td>Intrinsic Carrier concentration (cm⁻³)</td>
<td>1×10¹⁰</td>
<td>1.3×10⁷</td>
<td>2.1×10⁶</td>
<td>1×10¹⁵</td>
</tr>
<tr>
<td>Electron mobility (cm² V⁻¹ s⁻¹)</td>
<td>≤1400</td>
<td>≤5400</td>
<td>≤8500</td>
<td>≤40,000</td>
</tr>
<tr>
<td>Hole mobility (cm² V⁻¹ s⁻¹)</td>
<td>≤450</td>
<td>≤200</td>
<td>≤400</td>
<td>≤500</td>
</tr>
<tr>
<td>Thermal conductivity (W cm⁻¹ K⁻¹)</td>
<td>1.3</td>
<td>0.68</td>
<td>0.55</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 1.1: Some key material parameters of InP compared with other common semiconductors. All parameter values are from [16]. Values for InGaAs, InGaAsP and AlGaAs can also be found at the same link.
1.2 InP in Nanowire Form

The nanowire geometry brings in a number of advantages of its own. Orders of magnitude lower material usage, smaller device footprint, very high surface area (relative to the footprint and material volume), ability to tolerate higher level of strain without forming dislocations [36, 37] and freedom to form heterostructures in all three dimensions are some of them [38]. In addition to these, ensembles of nanowires behave as highly efficient light absorbers, trapping the incident light within the ensemble [39-42]. It has been shown that carefully designed InP nanowire arrays could absorb 94% of the incident light with energy above the band-gap [42]. Semiconductor nanowires could be used on their own, like in lasers [43-45], as templates to grow heterostructures and cavities [38, 46] or as building blocks to grow more complex structures [47]. They have not only been used in devices, but during the past decade, nanowires have also been instrumental in a number of key fundamental scientific discoveries [48, 49].

In nanowire form, the very low surface recombination velocity of InP makes it a standout. As the high surface-to-volume ratio is inherent in nanowire geometry, fast surface recombination would be undesirable in many applications [50, 51]. Furthermore, the thin native oxide of InP, that is normally formed when exposed to air is stable under operating conditions of most devices [52]. These two properties eliminate the need for additional passivation or cap layers to be grown on InP nanowires in order to enhance radiative recombination or prevent degradation, in contrast to GaAs and AlGaAs. Again, similar to the planar case, InP nanowires can be integrated with a large range of binary and ternary materials in axial and radial heterostructures. It should be noted here, due to the possibility of strain relaxation in the radial and axial directions (to a lesser extent) the range of materials with different lattice constants that can be grown without defects, is further expanded than in the planar case [36, 37, 53-56].

1.2.1 Demonstrated Applications of InP Nanowires

It could be seen that InP nanowire devices are not skewed to optical communications related applications as it is in the case of planar InP and related materials. The utilisation of InP nanowires and their heterostructures has spanned a large range of applications with some key significant advancements in the recent years. Light emitting diodes (LEDs) were among the early InP nanowire devices demonstrated [57, 58]. Field-effect transistors (FETs) [59, 60] and photodetectors [30, 61] are some of the other applications of InP nanowires that have shown promise. Deviating from conventional optoelectronics, recently, they have been used in applications aimed for quantum computing, such as single photon sources and entangled photon sources [58, 62-65]. Nanowire lasers are another area that has gained attention [43-45]. Note, that due to the very low surface recombination velocity of these nanowires [50], they have been able to be used as-grown without any passivation in these lasers.
InP nanowire solar cells [29-33] warrant a special mention. The three most recent reports [30, 32, 33] demonstrated close to or over 10% efficiency and that demonstrated in ref [33] is the highest reported efficiency for an array based nanowire solar cell [66]. This InP nanowire solar cell not only exceeded the ray optic limit by five times but also recorded the highest open-circuit voltage of 0.906 V, surpassing that of the best planar InP solar cell [67]. In addition to the above-mentioned characteristics, the high optical absorption coefficient [28], the band-gap of InP (which allows optimum absorption of the visible and near-infra red wavelengths where solar irradiance is also high) and the possibility to control the unnecessary parasitic layer and radial growth by in situ HCl etching [31, 68] have contributed to the success of InP nanowires in solar cell applications [29, 33]. Apart from the above, very recently, InP nanowires have been utilised in novel applications like water splitting [69] and hard x-ray detection [70].

1.2.2 Progress Made So Far in Relation to InP Nanowire Growth

Before proceeding to the discussion on the advances in growth, it is worth noting that arsenide and phosphide nanowires can grow in both zincblende (ZB) and hexagonal wurtzite (WZ) phases with controllable amounts of stacking defects, tuneable up to perfect structural quality. This is facilitated by the stacking sequence of ZB in <111> direction and will be further discussed in detail in Chapter 2.1. In the case of metal seeded VLS grown nanowires, the formation of a bilayer of a particular phase is governed by the interfacial energies between the particle, nanowire and the vapour phase [71]. InP has the lowest stacking fault energy out of all the common arsenide and phosphide III-V materials [72, 73]. This makes achieving pure crystal phase InP nanowires challenging as the phase could switch from one to another with small fluctuations in energy.

Resulting planar defects (twins in ZB and stacking faults in WZ) or mixed phase are not always detrimental. In fact, it could be seen from some of the above applications that they have not adversely affected the device, and in certain cases have even enhanced the device performance [44, 45, 59]. Stacking faults are even known to improve the mechanical properties of the nanowires [74]. On the other hand, in some applications, for example in single photon sources, phase purity is a must in order to maintain coherence for a longer time [64, 75].

Phase control has been one of the main challenges related to InP nanowire growth for some time. Even though pure WZ nanowires were able to be grown at high temperatures, the drawback was the high tapering that accompanied growth at high temperatures [76]. However, in the recent years, a number of groups have been able to demonstrate pure WZ phase Au seeded InP nanowire growth using various methods. Among these, Vu et al. have grown WZ InP nanowires using MOVPE at high temperatures while using in situ HCl etching to remove the tapering [77]. Tateno et al. demonstrated stacking fault-free WZ InP
nanowires for smaller Au particle sizes by increasing the V/III ratio [78]. Au seeded defect-free WZ InP nanowires have also been demonstrated using chemical beam epitaxy (CBE) [64, 79]. Naji et al. have demonstrated defect-free WZ InP nanowires growth by molecular beam epitaxy (MBE) on SrTiO$_3$(001) substrates [80].

Success has been much less in terms of achieving defect-free ZB InP nanowires. The highest level of control achieved up to date is the twinning superlattices, where the ZB structure is twinned periodically along the length of the nanowire. These have been achieved either by using large Au particles for the same high temperature growth conditions as pure WZ (and etching with HCl during growth) [77] or by doping with Zn [81].

In terms of optical properties, clean emission, limited to the free exciton and donor bound exciton transitions had been achieved for the MOVPE grown WZ InP nanowires by Vu et al., after the piranha cleaning of the nanowire side walls [77]. Similarly, after piranha etch, acceptor related emission have almost disappeared in the ZB superlattice nanowire spectra displaying clean free exciton emission with a 2.5 meV narrow line-width at 4 K [77]. Long carrier lifetimes between ~1 to 3 ns have been observed for these WZ and ZB nanowires for excitation powers between 64 nJ pulse$^{-1}$ and 21 μJ pulse$^{-1}$ at 4 K [77]. It should be noted that these optical properties have been measured without any passivation or shell growth around the InP nanowires.

1.2.3 Areas That Require Further Investigation in Relation to InP Nanowire Growth for Future Optoelectronic Devices and Associated Challenges

Almost all nanowires discussed so far have been grown homoepitaxially on InP (111)B substrates. It could be seen that considerable progress has been made and InP nanowire growth on InP (111)B substrates has almost reached its maturity in terms of growth, although there is plenty of room for exploration in terms of devices and applications.

However, if InP nanowires are to be integrated with well established Si technology so that complete, functional components can be designed on a single chip, they will have to be grown on Si substrates. Ideally, nanowires grown on Si substrates have to be of the same quality as those successfully demonstrated in above applications on InP (111)B substrates.

Numerous efforts have been made on InP nanowire growth on Si for more than a decade, but with limited success [31, 82-87]. Achieving high yield of vertical nanowires has been a constant problem and in some cases no epitaxial relationship is seen [82-86]. Quick oxidation of the Si surface, possible formation of anti-phase domains, existence of nanowires of <111>A and <111>B polarities, and lattice and thermal expansion coefficient mismatches are suggested as possible causes [82-84]. If Au is used to seed the nanowires, there is the additional problem of Au diffusing into Si and losing its shape [88]. Regardless, Au forms
mid-gap states in Si and hence, Au seeded nanowires that are directly grown on Si would not be a viable choice for future device applications [89].

Self-catalysed InP nanowires have been successfully grown on Si with 100% vertical yield by one group [90]. The small growth parameter space has been the limiting factor in this case. Thus, there are only very limited options for crystal and optical quality improvement and tuning.

Looking further into the future, it is known that the Si technology has actually evolved on Si (100) substrates and nanowires are almost the only type of basic structure that is grown on substrates with a different orientation. Therefore, in the long term, to complete the integration on a commercially viable level, the ultimate requirement would be for the nanowires to be grown on Si (100) substrates. This change of substrate orientation changes many aspects of nanowire growth from the well-known (111) substrates. Vertical growth on these substrates is a challenge for a start, as the preferred low energy directions would still be <111> [91-94]. The parameters space for the nanowire growth on [100] direction would be different and special care, in the form of pre-growth treatment or otherwise, will have to be taken in order to change the growth direction to the energetically unfavourable [100] direction [95-97].

Therefore, it is clear that growth on Si(100) would require a completely new knowledge base. However, hardly any research has been carried out on homoepitaxial vertical nanowire growth on any III-V (100) substrates (up until recently), let alone on Si(100). The properties such as facets and crystal structures of nanowires grown in a different direction would also be different. This in fact is more of an opportunity as opposed to a challenge. As discussed in Chapter 2.4, [111] oriented nanowires could have a limited range of facet profiles depending on growth parameters. Likewise, the [100] orientation would give rise to a different set of profiles that cannot be accessed by conventional [111] nanowires. Even the <111> and other growth directions observed on the (100) substrates could be looked at from a novel point of view to create unique nanowire-based ensemble structures [47, 98].

Growth of nanowires on (100) substrates brings forth another unforeseen advantage, especially for InP, for which pure ZB phase has been unachievable in the [111] growth direction. Achieving nanowires of both common phases is important as they have significantly different optical, (different band-gaps and electronic band structures) structural as well as mechanical properties [99]. In theory, the <100> oriented nanowires will have defect-free ZB crystal structure as the layer-by-layer stacking in the <100> direction prohibits a new layer from taking a WZ position, given that the nano-particle nanowire interface is perpendicular to the growth direction [96]. This scenario will be discussed further in Chapter 2.2.
Moving on to InP-related nanowire heterostructures, it could be seen that the focus has mainly been on only two materials, InAs and InAsP [53, 58, 62-64, 100-103]. The range of materials explored can be expanded to include other ternary and quaternary materials, especially the vast range that can be lattice matched as shown in Figure 1.1. III-V alloys such as InGaAs, InAlAs, GaAsSb and InGaAsP are some of such materials that allow band-gap variation over a wide range while maintaining a low lattice mismatch with InP. As mentioned earlier, in contrast to the planar case, reports on nanowire heterostructures targeting device applications in optical communications are relatively sparse [100]. Hence, there is plenty of room to investigate the nanowire counterparts of structures that have been well studied in the planar form and explore possibilities of incorporating the inherent advantages of the nanowire geometry in optical communications related applications.

### 1.3 Thesis Synopsis

This thesis presents a gradual advancement of growth of Au-seeded InP nanowires by MOVPE, in order to suit possible requirements for future optoelectronic device applications. It has investigated the progression from potential unexplored areas in growth on conventional InP (111)B substrates to growth on Si and finally, change of substrate orientation to suit industry standard [100]. Before proceeding to the main contributions, some relevant concepts related to nanowires are introduced in Chapter 2. A number of characterisation techniques have been used for the work presented in this dissertation and they are introduced in Chapter 3.

InP-In_{x}Ga_{1-x}As-InP radial quantum wells (QWs) emitting in the 1.3 μm wavelength range that are grown on InP (111)B substrates are investigated in Chapter 4. The QW tube structures are structurally and optically analysed using X-TEM, micro-PL and PL mapping. The QW emission is tuned in the 1.3 μm region by varying the QW thickness as well as composition. The optical behaviour of the nanowire QWs are modelled using the 8-band k-p model. Multiple quantum wells are also grown, demonstrating the potential to grow more complex structures.

Chapter 5 explores the growth of InP nanowires on Si (111) substrates using a thin buffer layer and thereby, facilitating the direct transfer of knowledge gained on growth on InP (111)B substrates to the Si substrate while eliminating direct Au contact with the Si substrate. A two-step approach is used to grow the thin buffer layer, and the growth conditions are optimised in order to achieve a smooth layer that covers the underlying Si substrate. The layer is characterised using a number of techniques and the nanowires are subsequently grown on the layer using the same growth parameters as those used for homoepitaxial growth. Nanowires grown under the same conditions on the buffer layer and InP (111)B substrates are compared morphologically and optically.
Chapter 6 proceeds to investigate the nanowire growth on InP (100) substrates, which is an unconventional orientation for nanowire growth. As mentioned previously, nanowires do not easily grow vertically on these substrates and the resulting nanowires generally seem random. This chapter classifies these nanowires into three types, namely vertical, non-vertical and planar, and investigates the growth directions, facets and the crystal structures of each type in detail. The non-vertical nanowires are found to be $<111>$ and $<100>$ oriented nanowires that inherit complex growth direction with respect to the substrate due to the 3-dimensional twinning that takes place during the initial stages. The growth directions with respect to the substrate are calculated using a mathematical model and verified by the measurements carried out on a large number of single nanowires.

The knowledge gained in Chapter 6 is used in Chapter 7 to control the relative yields of the vertical, non-vertical and planar nanowires. Growth parameters and pre-growth annealing conditions are tuned to achieve 87%, 67% and 100% of vertical, non-vertical and planar nanowires, respectively. The side facets of the $<100>$ oriented nanowires are engineered to form a range of facet profiles from square to octagonal cross-section shapes by tailoring the growth parameters and post-growth in situ annealing conditions. This is achieved while maximising the yield of vertical nanowires. Finally, the complex facets of $[100]$ nanowires are used to demonstrate their potential for novel opto-electronic applications by growing InGaAs QWs on them.

Finally, Chapter 8 discusses the overall conclusions of this work and suggests possible future research directions.

1.4 References


§ 1.4 References


Introduction


1.4 References


Introduction


Overview: This chapter introduces some of the key concepts that are used recurrently throughout this thesis. They are discussed in a general form here, while specific details pertaining to the work of each chapter are discussed in more detail in the relevant chapter.

2.1 Formation of Stacking Faults and WZ Phase in <111> Oriented Nanowires

Non-nitride III-V compound semiconductors (including InP) have zincblende (ZB) crystal structure in their bulk form. The ZB structure can be imagined as two interpenetrating face-centred cubic lattices of In and P atoms, respectively. The nearest neighbours of each atom are of the opposite type, forming tetrahedral binding. Figure 2.1 (a) shows the unit cell of InP. The stacking order of this structure in <111> direction shows a ABCABC... type repetitive pattern every three bilayers, as shown in the lower half of Figure 2.1 (b) and Figure 2.1 (c).

When nanowires are grown layer-by-layer in the [111] direction, each layer is formed independent of the previous layer, and therefore can take either position, other than the previous layer position, given that the formation energy is satisfied by the growth conditions [3]. For example after a stacking sequence of ABCA, the next layer could take the position of B or C. If B is selected, then the ZB stacking sequence will continue and if C is selected, then the stacking order would show mirror-like reversal after the last A plane: ABCAC.

It is interesting to see the options beyond this current point of ABCAC. The next layer could take a B position or an A position. If a B position is taken the sequence will be ABCACB, continuing the mirrored stacking sequence as shown in Figure 2.1 (b). Here the crystal will remain ZB and the A plane is called a “twin plane”, which is a common type of planar defect in [111] oriented nanowires. If the next layer take the A position, the sequence will change from a three-step repetitive pattern to a two-step pattern as ABCACA. This two-step pattern of CACACA... shown in Figure 2.1 (d) is not ZB crystal structure anymore, but hexagonal wurtzite (WZ) crystal structure. Therefore, the nanowires grown in [111] direction on ZB substrates can take WZ crystal phase.
Basic Concepts Related to Nanowires

In the CACACA... stacking sequence, a layer can occasionally nucleate in a B position, interrupting the sequence as CACACABACA. This B layer is called a stacking fault (indicated in Figure 2.1 (d)) which is also a planar defect in WZ nanowires. Note that

Figure 2.1: (a) Unit cell of InP. (b) ZB crystal structure with a single twin viewed along <110>. Note the reversal of stacking sequence at the marked twin plane. (c) Stacking sequence of ZB viewed along <111> direction, showing the three (A, B, C) unique positions. (d) Seamless ZB to WZ conversion of crystal structure and stacking fault formation in WZ. (e) Possibility to form twins, stacking faults and WZ phase in all <111> nanowires that grow off the substrate.

In the CACACA... stacking sequence, a layer can occasionally nucleate in a B position, interrupting the sequence as CACACABCACA. This B layer is called a stacking fault (indicated in Figure 2.1 (d)) which is also a planar defect in WZ nanowires. Note that
§ 2.2 Defect-Free ZB Phase Nanowire Growth in <100> Directions

the bold section in the previous sequence could also be looked at as a very thin ZB section. Similarly the CAC section in the twinned ZB sequence can also be looked at as a thin WZ segment.

It should be noted that other polytypes such as 4H or 6H can also form in [111] oriented nanowires when the relevant stacking sequence is maintained in the longer range [5-7]. As shown in Figure 2.1 (e), change of crystal structure is applicable not only to vertical nanowires but also to non-vertical <111> nanowires grown on (111), (100) or any other substrate, as the stacking sequence gains independence from that of the substrate once it is grown off the substrate.

2.2 Defect-Free ZB Phase Nanowire Growth in <100> Directions

In the case of [100] oriented nanowires (e.g., vertical nanowires grown on (100) substrates), given that the growth interface is perpendicular to the growth direction, the layer-by-layer growth implies that the growth takes place by nucleating and propagating (100) layers. These (100) layers are inclined to the ABCABC... stacking sequence of the substrate as shown in Figure 2.2 (a). Hence, each new (100) layer has a template structure which is determined either by the substrate (in the initial stages) or by the previous layer. Therefore, unless the particle is able to tilt inclined to the [100] growth direction or a dislocation is formed, the crystal structure of the ZB substrate is carried through the nanowire irrespective of the growth conditions. This is equally applicable to non-vertical <100> nanowires.

As mentioned earlier, this situation changes if the nano-particle is able to tilt with respect to the growth direction, so that the growth interface is parallel to the {111} planes as

![Figure 2.2: (a) Layer-by-layer stacking in [100] oriented nanowires with the nano-particle-nanowire interface perpendicular to the growth direction. (b) A [100] oriented nanowire with nano-particle tilted such that the nano-particle-nanowire interface is parallel to the {111} planes.](image)
shown in Figure 2.2 (b). Twin formation by tilting of the particle is further discussed in Chapter 7.5.

2.3 Polarity of Facets in Compound Semiconductors

In the crystal lattice of compound semiconductors (ZB, WZ or any other phase), some facets could consist of only one type of atoms. For example, the surface of (111) planes could be terminated with either only In or P atoms in the case of InP. These are noted as (111)In or (111)A and (111)P or (111)B, respectively. It is also common to define the notation within the crystal so that (111) is an In terminated facet, which makes the opposite facet, that is (-1-1-1) a P terminated facet. These are called ‘polar’ facets. Similarly in the WZ structure, (0001) and (000-1) are such polar facets. (111)A and B surfaces of ZB InP are shown in Figure 2.3 (a).

Not only the type of atoms, but also the dangling bonds and hence the surface reconstruction could be different in these differently polar surfaces. For instance, each P atom of the (111)B surface would have a lone pair of electrons, while In atoms of the (111)A surface will not have any unbound electrons as all three electrons on its outer shell have contributed in forming the bonds with the P atoms below. Hence, the polarity of planes also induces differences in reactivity, surface reconstruction, surface energy and growth rate [8-13].

Figure 2.3: (a) Stick and ball view along <110> and space filled top view along <111> of InP, showing In terminated (111)A surface and P terminated (111)B surfaces. (b) Respective (111) and (-1-1-1) surfaces of Si, showing identical surface atoms. (c) Partially polar (112)A and (112)B surfaces of InP along with respective tilted space filled models for clarity. The surface atoms are marked by yellow circles in each case, showing two out of three atoms being In in the case of (112)A and P in the case of (112)B.
Some facets may contain atoms of both elements, but in unequal numbers. One example is the (112) facets that is shown in Figure 2.3 (c), where the elements are at a 2:1 ratio. Using the same notation as above, surfaces with 2/3 of In atoms are denoted as (112)A and those with 2/3 P atoms are denoted (112)B. These surfaces are called ‘partially polar’ surfaces. Similar to fully polar surfaces, these too, show differences in reactivity and growth rates. If a surface has an equal number (1:1) of the two types of elements, they are called ‘non-polar’, and (100) and (110) in ZB and (11-20) in WZ are examples of such facets.

On the same note, such polarities do not exist in elemental semiconductors such as Si and Ge, as all atoms are uniform throughout the crystal. (111) and opposite (-1-1-1) surfaces of Si are also depicted in Figure 2.3 (b) for comparison.

2.4 Common Low-Index Side Facet Combinations and Cross-Sectional Shapes of Conventional [111] Oriented Nanowires

Nanowire side facets generally belong to low-index facet families that are parallel to the growth axis. In the case of ZB [111] nanowires, {110} and {112} facet families are commonly seen. Figure 2.4 (a) shows the directions in ZB and WZ crystal structures with respect to the ZB (111) substrate that [111]/[0001] nanowires are commonly grown on. In ZB phase, the {110} facets are non-polar and equivalent, therefore the resulting cross-section shape is symmetric equilateral hexagonal. {112} facets could also result in equilateral hexagonal shapes. However, the six facets that form the hexagon are not identical. They consist of three {112}A facets and three {112}B facets that have opposite partial polarities as discussed previously. Therefore, depending on the growth condition, one type may grow faster than the other resulting in a truncated triangular cross-section shape [14]. MOVPE nanowires growth is mostly carried out under high V/III conditions and facets with type A partial polarity grow faster under these conditions [9, 12, 14], resulting in smaller {112}A facets and larger {112}B facets. In the extreme case, the {112}A facets may complete their over growth resulting in a triangular cross section shape, consisting of three {112}B facets.
Basic Concepts Related to Nanowires

Table 2.1: Common low-index facet combinations and cross sectional shapes of [111] oriented nanowires.

<table>
<thead>
<tr>
<th>Facet combination</th>
<th>Cross sectional geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Six ${110}$ facets (ZB)</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>2  Six ${112}$ facets (ZB)</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>3  Three ${112}$ facets (ZB)</td>
<td>Triangular</td>
</tr>
<tr>
<td>4  Six ${11-20}$ facets (WZ)</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>5  Six ${1-100}$ facets (WZ)</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

Similarly, WZ phase nanowires have $\{11-20\}$ and $\{1-100\}$ (a- and m-planes in WZ crystal structure, respectively) type side facets. Both these families are non-polar and therefore the six facets of each family are equivalent, resulting in an equilateral hexagonal cross-section shape. Common facet profiles of [111] oriented nanowires discussed so far are summarised in Table 2.1.

It should be noted that some nanowire side facets could be much more complicated than those discussed above. For example, the facets of twinned superlattice nanowires are made of alternating $\{111\}$ octahedral segments and show a saw-tooth-like morphology from the side [15, 16]. The $\{112\}$ faceted, truncated triangular cross-sectioned nanowires may appear to change its relative truncation as elaborated in references [14] and [12]. This is due to the change in relative position of the fast growing $\{112\}$A facets with effective 180° rotation at each twin plane. The major nanowire facets could be composed of other nano-
scale facets, like in the case of \{112\} facets, where it can be considered as a combination of \{111\} and \{100\} nano-facets [14]. Nano-facets could even be formed along the nanowire due to tapering as shown in Figure 2.4 (b). However, these complex scenarios that occur along the nanowire are not considered in Table 2.1, which discusses only the primary facet profiles.

### 2.5 Growth of Lattice Mismatched Nanowire Based Structures

When a material with a different lattice parameter to the substrate is epitaxially grown, it needs to expand (contract) in the direction lateral to the growth direction and contract (expand) in the growth direction in order to accommodate the mismatch in the lattice size as shown in Figure 2.5 (a). Depending on the lattice mismatch, mechanical properties of the layer material and thickness, in most cases dislocations may form, when the layer is above a certain critical thickness as shown in Figure 2.5 (b) [17]. These are highly undesirable in semiconductor devices as they introduce rows of missing or dangling bonds. In the case of layer structures, the grown layer could relax only in the growth direction as it is restricted in the other two dimensions. This increases the necessity to form dislocations in order to relieve the strain.

In the case of nanowires (specially, those with smaller diameters), the nanowire material can expand or contract also in the directions perpendicular to the growth direction as shown in Figure 2.5 (c). This allows it to relieve mismatch strain rather coherently and
materials with larger lattice mismatch to grow epitaxially without forming misfit dislocations compared to the planar case [18-21]. Strain can be more coherently relieved in nanowires with smaller diameters and analogous to the critical thickness of the planar case, the largest diameter that relaxation could take place without forming misfit dislocations is called the critical diameter [18-21]. This depends on the size of mismatch and mechanical properties of the material similar to the planar case [18, 19, 21]. For example, it has been seen that GaAs nanowires with small diameter could grow without forming any dislocations while InGaAs and InAs nanowires with larger diameters and larger lattice mismatch formed dislocations when grown on Si by selective area epitaxy [22-24].

This advantage of the nanowire geometry is further exemplified in the case of axial heterostructures. Here, the possibility of dislocation formation is even less than in the case of growth on lattice mismatched substrates, as both segments of the axial heterostructure can now contribute to accommodate the mismatch as shown in Figure 2.5 (d) [18, 19, 21]. Again, this is limited by the level of mismatch and the diameter. Dislocations in axial heterostructures are commonly seen in those grown under extreme lattice mismatch like InSb/InAs and GaSb/GaAs [25].

**Figure 2.5**: (a) Expansion and contraction of the lattice when a layer is grown on mismatched substrates. (b) Formation of misfit dislocations in layers with smaller and larger lattice parameters to the substrate. (c) Lateral relaxation of mismatch strain in nanowires with different lattice parameters compared to the substrate. (d) Efficient relaxation of mismatch strain in axial nanowire heterostructures by contribution from both segments.
2.6 Direct and Indirect Band-Gaps of Semiconductors

If the maximum of the valence band and the minimum of the conduction band in the band structure have the same momentum \( (k) \) value, then that semiconductor is said to have a direct band-gap (see band structure of ZB InP in Figure 2.6 (a)). If the momentum \( k \) is different, the band-gap is indirect as shown in band structure of Si in Figure 2.6 (b). Both, energy and crystal momentum need to be conserved in the process of recombination of electrons and holes. Hence, in the case of direct band-gap materials, the recombination could take place solely by emitting a photon. This direct process can take place easily and fast with a high proportion of total recombinations being radiative. Therefore, direct band-gap materials have high radiative recombination efficiencies.

In the case of the indirect band-gap, conservation of crystal momentum needs to be satisfied by mediation of a phonon, in addition to the photon as shown in Figure 2.6 (b). This involvement of a phonon makes the occurrence of this two-step process slow and less likely within a given time span, and other means of non-radiative recombination, such as recombination at defects and grain boundaries become more likely. Therefore in indirect

![Figure 2.6: (a) Band structure of ZB InP (direct band-gap). (b) Band structure of Si (indirect band-gap). Illustrations are largely adapted from [1].](image-url)
band-gap materials, the proportion of radiative recombinations with respect to the total number of recombinations is low. Converse is also true in the process of light absorption, with indirect band gap materials requiring the simultaneous mediation of a phonon together with the photon. For this reason, direct band-gap materials are used to fabricate the active regions of devices that involve light absorption or emission such as lasers, light emitting diodes, photodetectors and solar cells.

### 2.7 Band Structures of ZB and WZ InP

The difference in crystal structure also leads to differences in electronic band structure in the crystal phases. Here, the band structures of the two most commonly seen phases in InP nanowires, that is ZB and WZ are compared. The hexagonal WZ crystal system has lower symmetry compared to cubic ZB, which results in some degeneracies in the band structure being lifted. On the other hand, due to the similarities in the crystal systems (which can be better understood when viewed along the <111> direction as discussed in Section 2.1), many of the high symmetry points in the Brillouin zones are related [29].

Figure 2.7 (a) and (b) show the ZB and WZ InP band structures at the Γ point, respectively. Both have direct band-gaps. The parameter values of ZB are well studied and have been known for years as it is the phase that exists in bulk form [2]. WZ phase of non-nitride III-V semiconductors have only come to notice in nanowire form and there are some discrepancies in values measured by various groups using varied techniques. However, for InP, it is well agreed that the WZ band-gap is about 70 meV larger than that of ZB [4, 30-33]. Reported values of some important parameters are compared in Table 2.2.

![Figure 2.7](image.png)

**Figure 2.7:** Band structures of, (a) ZB InP and (b) WZ InP at the Γ point. Values of ZB InP are from ref [2] and WZ InP are from ref [4]. (c) Type II band alignment between ZB and WZ InP.
Quantum Confinement and Nanowire-Based Quantum Heterostructures

Quantum confinement is achieved by restricting the movement of carriers in one or more dimensions to a length comparable to the de Broglie wavelength of the carriers. When the carriers are restricted in one dimension, the structures are called quantum wells (QWs), when restricted in two dimensions they are called quantum wires (QWRs), and when restricted in all three dimensions, structures called quantum dots (QDs) are formed. One of the main consequences of quantum confinement is the change in the density of states (DOS – which can be understood as number of quantum states per unit energy), and engineering the DOS is a main objective of considering these structures. Figure 2.8 (a) shows how the DOS changes with confinement. As the number of dimensions of confinement increases, the DOS become more discrete, quantizing the energy levels that the electrons and holes could take.

As can been seen from the relative positions of the valence and conduction bands in Figure 2.7 (a) and (b), and Figure 2.7 (c), the alignment between the ZB and WZ InP is of Type II, where both, the conduction and valence band edges of WZ are higher than those of ZB [36]. This results in electrons and holes being spatially separated into ZB and WZ regions, respectively in such ZB-WZ junctions.

2.8 Quantum Confinement and Nanowire-Based Quantum Heterostructures

Table 2.2: Reported experimental and theoretical values of some key parameters related to WZ InP band structure at the Γ point. All values are for low temperatures (~4 - 10 K).

<table>
<thead>
<tr>
<th>Reference</th>
<th>$E_A$ (eV)</th>
<th>$E_B$ (eV)</th>
<th>$E_C$ (eV)</th>
<th>$\Delta_{so}$ (meV)</th>
<th>$\Delta_{cr}$ (meV)</th>
<th>$E_{WZ(A)} - E_{ZB(A)}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gadret et al. [4]</td>
<td>1.488</td>
<td>1.532</td>
<td>1.675</td>
<td>84</td>
<td>147</td>
<td>64</td>
</tr>
<tr>
<td>Alouane et al. [34]</td>
<td>1.490</td>
<td>1.530</td>
<td>1.669</td>
<td>74</td>
<td>145</td>
<td>66</td>
</tr>
<tr>
<td>Perera et al. [33]</td>
<td>1.508</td>
<td>1.538</td>
<td>1.670</td>
<td>52</td>
<td>140</td>
<td>84</td>
</tr>
<tr>
<td>De Luca et al. [32]</td>
<td>1.493</td>
<td>1.537</td>
<td>1.673</td>
<td>84</td>
<td>139</td>
<td>69</td>
</tr>
<tr>
<td>Tuin et al. [31]</td>
<td>1.493</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Vu et al. [30]</td>
<td>1.491</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>De et al. [29]</td>
<td>1.474</td>
<td>1.537</td>
<td>1.673</td>
<td>108</td>
<td>303</td>
<td>50</td>
</tr>
<tr>
<td>Dacal et al. [35]</td>
<td>1.494</td>
<td>1.539</td>
<td>1.737</td>
<td>78</td>
<td>210</td>
<td>70</td>
</tr>
</tbody>
</table>

1 Band-gap of ZB InP is taken to be 1.424 eV as per Vurgaftman, et al. Journal of Applied Physics, vol. 89, pp. 5815-5875, 2001
2 Experimental
3 Theoretical
Experimentally, these structures are fabricated by confining a lower band-gap semiconducting material within a higher band-gap material, so that the carriers are confined to the lower band gap material. The quantum confined structures (QWs, QWRs or QDs) are created by using various techniques such as patterning and self-assembly. With the modern epitaxial growth techniques like MOVPE and MBE, it is possible to achieve atomically sharp interfaces in these, forming high quality heterostructures. Discrete electronic energy states and other advantages such as the ability to grow strained structures, emission tunability and sharpness, and the possibility of obtaining higher gain (in lasers) make quantum confined heterostructures a popular choice for devices over bulk materials.

The three dimensional geometry of nanowires provides many interesting options for the design of nanowire-based quantum confined structures. Given that the nanowire diameter is large enough, QWs can be grown in the axial direction in the form of discs as shown in Figure 2.8 (b) [39]. Core-shell QWs can also be grown in the radial direction forming tubular wells (see Figure 2.8 (b)ii) [39]. These can also be repeated to form multiple QWs as...
shown in Figure 2.8 (b)iii and iv. If the nanowire diameter is small enough to be comparable to the de Broglie wavelength of the carriers, a thin nanowire on its own would form a QWR. This could be clad in another higher band-gap material depending on the application as shown in Figure 2.8 (c)i. Alternatively, QWRs could be grown on the apices of a thicker nanowire [40], making use of preferential material growth on certain facets as depicted in Figure 2.8 (c)ii.

There are number of ways to incorporate QDs in nanowires. As shown in Figure 2.8 (d)i, if the nanowire core is sufficiently thin, they could be grown as axial segments. Stranski-Krastanov QDs can also be grown on the side walls of the nanowires [41] (see Figure 2.8 (d)ii). Recently, there have been reports of high quality self-assembled QDs in GaAs-AlGaAs core-shell nanowires, formed due to complex segregation patterns of Al in the AlGaAs shells [38, 42]. A review on most of these nanowire based quantum structures can be found in ref [39].

2.9 Summary

This chapter discussed some of the structural and optical aspects of nanowires that are most relevant to the content discussed in the following chapters of the thesis. The basic concepts related to the structural aspects included stacking faults and WZ phase formation, polarity, nanowire facets and growth of lattice mismatched nanowire-based structures. Types of band-gaps, band structures of ZB and WZ InP, and quantum confinement in nanowire-based structures were discussed in relation to optical aspects.

2.10 References


Basic Concepts Related to Nanowires


§ 2.10 References


Chapter 3

Experimental Techniques

Overview: This chapter discusses the experimental techniques and procedures used throughout the dissertation for sample growth, and structural and optical characterisation. Only the basic principles of each technique and specific details pertaining to the work presented in this dissertation are discussed here.

3.1 Metal Organic Vapour Phase Epitaxy (MOVPE)

Metal Organic Vapour Phase Epitaxy (MOVPE) is one of the most commonly used epitaxial semiconductor growth techniques with the ability to grow high purity materials with sharp interfaces. The absence of ultra-high vacuum requisite is another advantage of MOVPE over other common growth techniques such as molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE). The relatively fast growth rate and scalability have led to wide-spread use of MOVPE in the industry [1]. Just as the name suggests, metalorganic compounds are used as sources; e.g., trimethylindium (TMIn), triethylindium (TEIn), trimethylantimony (TMSb) and diethylzinc (DEZn). These exist in liquid or solid state under normal operating conditions. The other type of sources is the hydrides such as arsine (AsH₃), phosphine (PH₃) and silane (SiH₄) which are inorganic and are in gaseous form.

All nanowire growths discussed in this dissertation have been carried out using the MOVPE technique in an AIXTRON 200/4 horizontal flow reactor. Figure 3.1 shows a schematic diagram of this system. TMIn, TMGa, AsH₃ and PH₃ were used as precursors for the two materials, namely InP and InGaAs, discussed in this work. Ultra-high purity H₂ gas was used as the carrier gas and nanowire growths were normally carried out at 100 mbar pressure. The growth pressure was raised to 180 mbar for the growth of radial quantum wells. The total flow rate maintained during growth was 15 standard litres per minute. The reaction chamber of the MOVPE system consists of a rotating graphite susceptor and is heated by three sets of infrared lamps with independently adjustable power settings. The exhaust gases that contain by-products and unreacted precursors are passed through a number of filters and a charcoal scrubber which reacts with the toxics before being released to the atmosphere.
Figure 3.1: A schematic of the Aixtron 200/4 MOVPE reactor system.

\[
\text{In(CH}_3\text{)_3 + PH}_3 \rightarrow \text{InP + 3CH}_4 \quad (3.1)
\]

\[
(x)\text{In(CH}_3\text{)_3 + (1-x) Ga(CH}_3\text{)_3 + AsH}_3 \rightarrow \text{In}_x\text{Ga}_{1-x}\text{As + 3CH}_4 \quad (3.2)
\]

Equations (3.1) and (3.2) show the idealised reactions to grow InP and InGaAs. However, it is known that these reactions are not as straightforward, but take place over a number of intermediate steps. The precursor decomposition begins in the gas phase and the final reaction is completed on the substrate surface [1-5]. The intermediate steps and by-products greatly vary with many parameters such as temperature, pressure, carrier gas and substrate [1-5].

3.1.1 Vapour-Solid (VS) Growth in MOVPE

The reactions discussed above are directly linked to the epitaxial crystal growth from the reactants in the vapour phase, and is the conventional mechanism of growth in MOVPE. Ideally, material deposition takes place layer-by-layer on the existing substrate continuing its atomic arrangement. Epitaxial, but not ideal layer-by-layer, other VS growth modes such as Volmer-Weber (VW) and Stranski-Krastanow (SK) have their own uses such as in quantum dot growth. VS growth is normally carried out at high temperature (>500 °C) to ensure good crystal quality and morphology.
§ 3.1 Metal Organic Vapour Phase Epitaxy (MOVPE) 35

VW as well as layer-by-layer (Frank-van-der-Merve - FM) VS growth modes are observed in the work presented in this thesis related to InP growth on Si. Details of the growth conditions and results are presented in Chapter 5. VS growth is also used for the growth of the radial quantum wells around the nanowires. After the nanowire core growth (discussed in the next section), the temperature is ramped up to typical VS growth temperatures (550 °C in this case) to continue quantum well and barrier growths. It should be noted that in the case of nanowire radial heterostructures, the virtual ‘substrate’ for the epitaxial growth is perpendicular to the conventional layer case. Therefore adatoms absorbed and migrating on two perpendicular surfaces (as shown in Figure 3.2) could contribute to the growth, complicating the growth compared to planar case [6-8]. Furthermore, the type of facet (orientation) of these perpendicular surfaces could be different from that of the substrate and the facets of a single nanowire could also be non-uniform, leading to different growth rates compared to the planar substrate and between the different facets [9-11]. Possible implications of these on quantum well growth are discussed further in Chapter 4 and 7.

In addition, the unintentional VS growth that takes place on the side walls of the nanowires during its core growth gives rise to tapering, and plays a role in forming their cross-sectional profiles, as discussed in Chapters 6 and 7.

3.1.2 Vapour-Liquid-Solid (VLS) Growth in MOVPE

One dimensional nanowires are mostly grown with the aid of a metal seed particle due to advantages such as the ease of achieving one dimensional growth, the controllability of dimensions and position, the ease of controlled growth of heterostructures, and in most cases, the easy scalability. Self-seeded and foreign metal seeded are the two main variants and Au is the most commonly used foreign seed particle metal; although other metals such as Pd, Ni, Ag, Cu, Pt have been studied (see [12] and references therein). All InP nanowire cores discussed in this dissertation are seeded by Au particles.

Figure 3.2: Adatom absorption and diffusion on (a) planar surfaces, (b) nanowire side walls.
Growth mediated by Au (or any other foreign metal) particle is slightly different to VS growth discussed above. As shown in Figure 3.3, when the particles are heated on the substrate, it could form a eutectic alloy with it, which would be Au-In in the current case. With further precursor supply, the particle becomes supersaturated and starts precipitating material at the particle substrate interface. In the case of arsenide and phosphide III-V materials, it is the group III that is mostly absorbed in the particle as the solubility of group V (As and P) in Au is known to be low [13-15]. Group V was thought to be incorporated mostly through the boundary of the particle-nanowire interface (triple phase boundary – TPB) while some studies had suggested a similar mechanism to group III [14, 16]. However, in the recent years it has been confirmed that a low, but critical fraction of group V is directly absorbed into the droplet, and this greatly influences its chemical potential and hence the crystal phase [17-19]. The continued precipitation of III-V pairs at the interface with continued precursor supply ensures the anisotropic one dimensional growth.

As the growth is being carried out via a liquid phase, this mechanism is called vapour-liquid-solid (VLS) growth mechanism. VLS growth can also be carried out in other growth systems such as CBE, MBE and MOMBE (metal organic MBE) [20-28]. The growth temperature used for VLS growth in MOVPE is generally lower (around 350 – 500°C) than those used for VS growth. The exact growth parameters and procedures used for the VLS growth of nanowire cores presented in this dissertation will be elaborated in the relevant chapters.

It should be noted here that there are still some open questions regarding the role of the Au particle. In some cases, it has been shown that it remains solid, while still acting as a preferential growth site leading to vapour-solid-solid (VSS) type nanowire growth [13, 15, 16, 29-34]. While it has traditionally been believed to be acting as a catalyst, there is now doubt as to whether it actually reduces the activation energy of the reaction to be called a

**Figure 3.3:** VLS growth process of nanowires.
chemical ‘catalyst’, or it is merely acting as an aggregation site for the reactants [34-38] in the capacity of a rather vaguely defined ‘physical catalyst’ [15].

3.1.3 Sample Preparation for Nanowire Growth

The substrates (or buffer layers in Chapter 5) were first immersed in a 0.1% poly-L-lysine (PLL) solution for 1 min to create a positively charged layer on the surface [39]. After rinsing with de-ionised (DI) water and drying, the negative surface charged Au metal particles were dispersed on the PLL-coated substrates. These were colloidal particles (obtained from Ted Pella Inc.) with diameters of either 30 or 50 nm (as specified in each chapter) that are suspended in water, having trace amounts of citrate, tannic acid and potassium carbonate [40]. After a deposition time of 30 s the samples were rinsed once more with DI water and dried with a N₂ gun.

The PLL deposition step is important to ensure even distribution, high adherence of the Au particles to the substrate surface and prevention of agglomeration of particles before growth. The areal density of the particles deposited on the substrate can be controlled by either diluting the Au particle solution in DI water or by varying the deposition time.

3.2 Electron Microscopy

Electron microscopes use a beam of electrons to create the image of a sample just as conventional light microscopes use light. The resolution of the light microscope is generally limited by the wavelength of light to about 200 nm (except in the case of super-resolution microscopy). Hence electrons, which have a smaller wavelength than light, are used in electron microscopes to achieve better resolution.

The sample-electron interaction produces a number of different types of signals such as secondary, backscattered and Auger electrons as well as visible light and X-rays as shown in Figure 3.4. If the sample is thin enough, electrons may pass through the sample scattering the electrons elastically or inelastically. These different signals can be used to either enhance the details in the image, as in the case of high angle annular dark field (HAADF) imaging that will be discussed under Section 3.2.2, or to extract the complimentary information to imaging, such as composition (using X-rays) or emission wavelengths (using the visible light or photons that are emitted). This vast range of characterisation capabilities related to electron microscopy makes it a very powerful technique in the field of nanotechnology.

It should also be mentioned, that due to the use of high energy electrons, electron microscopy analysis may also produce artefacts such as beam damage, edge enhancement and charging effects, which need to be kept in mind and taken into account during analysis.
There are two main electron microscopy varieties namely, scanning and transmission electron microscopy that are loosely analogous to the reflected (or incident) and transmitted light modes in optical microscopy. The following two sections discuss these two techniques in more detail.

### 3.2.1 Scanning Electron Microscopy (SEM)

SEM can be used for imaging as well as for other types of analysis mentioned earlier, with the required detectors and hardware fitted coupled to the main system. Only the imaging functionality is discussed in this section and the energy dispersive X-ray spectroscopy (EDX) analysis in the SEM system will be discussed in Section 3.4.

The basic operation of the SEM is accomplished by raster scanning a focused electron beam on the sample surface. The secondary electrons (SEs) and backscattered electrons (BSEs) produced can be used for imaging purposes. The lower energy (<50 eV) SEs are produced by ejection of weakly bound outer shell electrons of the atoms of the specimen by the irradiating electrons. The SEs created deeper in the sample are reabsorbed by the sample and only those produced on the surface of the sample (5-50 nm, depending on the sample and operating conditions) escape to reach the SE detector commonly placed above the sample towards the side. Hence the SE image gives details about the surface topology of the sample. As shown in Figure 3.5, the volume of material contributing to the SE generation changes depending on the contours of the surface. This controls the number of SEs reaching
the detector during the scans and hence the contrast, creating the grey scale images. Since SE imaging only involve the surface of the sample, generally low to moderate (< 20 kV) accelerating voltages are used for the scanning electron beam.

Almost all SEM images in this thesis are SE images. A Zeiss Ultra Plus field emission gun SEM (usually operated around 2-7 kV) and the SEM functionality in a FEI Helios 600 NanoLab focused ion beam system (usually operated 1-5 kV) were used for this work. The beam is deflected in the horizontal and vertical directions in order to carry out the raster scan. The sample stage is able to be move, tilt and rotate with respect to the beam so that features can be imaged and analysed in multiple viewing directions. These functionalities are extensively used in the work presented in Chapter 6.

The other type of emitted electrons, that is BSEs, are actually electrons originated from the beam that are reflected back (backscattered) after interaction with the atoms of the sample. Since heavy elements with higher atomic numbers can backscatter electrons better, these will give a brighter contrast in the BSE image compared to lower atomic number elements. Hence, BSE imaging is used to detect compositional variation in the sample. As few such electrons are produced during scanning, the BSE detector is placed in the SEM column directly above the sample, around the electron beam (in a doughnut shape). The solid angle of collection of BSEs is maximised in this fashion. SE and BSE electron images are usually used side-by-side in order to gain a complete understanding of topology and composition.

Electron microscopy samples in general, should be conductive in order to prevent electrostatic charge accumulation. Electrically insulating samples are usually coated with a thin carbon or Au layer in order to make them conducting. No such sample preparation was carried out in this work as InP and Si semiconducting materials were conductive enough to prevent any charging problems.

![Figure 3.5: Interaction of electron beam with the sample in SEM.](image)
3.2.2 Transmission Electron Microscopy (TEM)

As the name implies, this technique passes a high energy electron beam through an ultra-thin sample in order to achieve its functionality (which is not just limited to imaging). The electrons interact with the sample in many ways as it passes through; hence, with the appropriate equipment configuration, diffraction, electron energy loss, electron phase change, elastic and inelastic scattering of electrons can be used to extract a wealth of information on crystal structure, morphology, defects, strain and composition. This discussion will be limited only to the functionality used for the work presented in this dissertation.

Figure 3.6: Ray diagrams of TEM in, (a) diffraction mode, (b) imaging mode. Adapted from [41].
As shown in Figure 3.4, the three main types of electrons produced by their transmission through the sample are, minimally altered direct electrons, and elastically and inelastically scattered electrons. Bragg scattering by the crystal planes parallel to the incident electron beam gives rise to diffraction spots at the back focal plane as shown in Figure 3.6 (a) and (b), which depicts simplified ray diagrams of TEM in two basic modes, namely diffraction and imaging. The patterns formed by these spots (diffraction patterns) are different depending on the type of planes that are parallel to the electron beam. Hence these, viewed on the phosphor screen in the diffraction mode (Figure 3.6 (a)) are used to tilt the sample and align it in the required angle before imaging.

### 3.2.2.1 Diffraction

In addition to being an aid in tilting the samples to the required viewing angle, the diffraction patterns contain other valuable information in reciprocal space about the sample. The pattern profile can indicate the crystal phase while the distance between the spots can be used to measure the lattice constant, hence the strain and composition of a known compound. Additional spots, satellite spots and streaking of spots could indicate extended planar defects such as stacking faults and mixed phase. The relative orientation of the indexed diffraction pattern compared to the image can be used to ascertain the crystal growth direction as in the case of nanowires.

When carried out with a converged beam on the sample, the diffraction pattern results in discs instead of spots. The patterns formed inside these discs can be used to gauge the thickness and the polarity with the help of simulations.

Two TEMs, a Philips CM 300 operated at 300 kV and JEOL 2100F operated at 200 kV have been used for the work presented in this dissertation. Diffraction functionality in both machines have been used for alignment of sample and determination of crystal phase in Chapters 4 to 7, confirming epitaxial growth of InP layers on Si in Chapter 5, and confirming the growth direction of <111> oriented nanowire in Chapter 6.

### 3.2.2.2 Bright-field and dark-field imaging

Bright-field imaging is the most commonly used functionality of TEM. An aperture called objective aperture can be inserted at back focal plane (see Figure 3.6 (b)) to select the set of beams one would like to be used to create the image in imaging mode. For example, if the direct (undiffracted) beam is selected, then the image would contain contribution from all electrons that went through the sample without diffracting. This would also include electrons that passed through areas that no sample was present, leading to a bright background and hence the name ‘bright-field’.
Scattering of the electrons will be different depending on the material (elements with higher atomic number will scatter more) giving rise to Z-contrast in bright-field images. Areas with higher thickness will also appear darker due to scattering and as fewer electrons could escape thick regions without getting absorbed compared to thin ones. Bright-field images can also be created without using any aperture since the proportion of diffracted electrons is much less than those pass directly. However the contrast of the image will be much lower. All TEM images presented in this work (nanowires, layer and their cross sections) are bright-field images.

Similarly if a spot or a collection of spots other than the direct beam is selected at the back focal plane, then the image is created only with the contribution from electrons diffracted from regions pertaining to those relevant spot/spots. In this case, the background will be dark, since the undiffracted beam is blocked. The area which contributed to the selected spot/spots will be bright, forming dark-field images. Spot/spots arising from a different material or phase can be used for this. Conversely, the areas in the sample that give rise to unknown diffraction spots can also be identified using dark-field imaging.

### 3.2.2.3 High Resolution TEM (HRTEM)

HRTEM uses the phase difference between the direct beam and the diffracted beams to form an interference image. This phase contrast image can translate down to individual columns of atoms. HRTEM images are obtained by tilting to exact zone axis, and imaging under high magnification and very fine focus with no or large objective aperture that allows as many beams (including the direct beam) to pass through. The fact that details down to the placement of individual atom columns can be seen makes this a very powerful technique. It can be used on its own or complementarily with diffraction patterns in order to study interfaces and grain boundaries, identify phase, planar defects, strain, lattice constant and dislocations.

In the work presented in this thesis, HRTEM has been routinely used in both the above mentioned machines for precision atomic level measurements such as quantum well thicknesses, InP-Si (in layers) and InP-InGaAs (in nanowire quantum wells) interface analysis, strain mapping, nanowire crystal phase, and planar defect studies.

### 3.2.2.4 Scanning Transmission Electron Microscope (STEM) and High Angle Annular Dark Field (HAADF) imaging

STEM is a mode available in some TEMs where the electron beam is focused to a small spot and raster scanned over the thin sample. The raster scanning functionality enables characterisation techniques like EDX mapping, HAADF imaging and electron energy loss spectroscopy given the appropriate detectors are available. HAADF imaging and EDX
mapping has been used in the work presented in this thesis and HAADF imaging will be discussed here while EDX mapping will be discussed in Section 3.4.

As stated previously, the scattering of electrons is highly sensitive to the atomic number (Z) of the atoms in the sample (approximately proportional to Z^2). The forward scattered electrons that are scattered out to high angles (generally ~>3°) [41] are collected using a ring-shaped detector while raster scan is being carried out in STEM mode on the sample in order to form the HAADF images. As the direct beam is avoided, this will be a form of dark-field imaging, but the contrast arising from difference in atomic numbers is much higher than other forms of imaging. Figure 3.7 shows a schematic of the STEM mode operation and HAADF detector.

STEM mode is available in the JEOL 2100F out of the two TEMs used in this work. HAADF imaging has been used for the InGaAs quantum well tube study (shape and interfaces) presented in Chapters 4 and 7. One such example is shown in Figure 4.1 (d). The STEM probe sizes used for these studies were 0.5 and 0.7 nm. The HAADF imaging related to this work was performed in collaboration with Dr. Yanan Guo.

### 3.3 Sample Preparation for TEM

As mentioned earlier, the electrons need to pass through the sample in order to be analysed by TEM. Hence, the samples should be thinner than ~100-200 nm depending on the TEM operating conditions and material. Thickness should be even less for high resolution imaging, ideally less than about 70 nm. Special techniques are employed to prepare TEM samples so that they are thin, clean and free of sample preparation artefacts. Traditional
mechanical polishing techniques such as tripod polishing and dimple grinding, chemical etching, small angle cleavage, and focused ion beam (FIB) are some of them. The next three sub-sections discuss the techniques used to prepare TEM samples for the work presented in this dissertation.

### 3.3.1 Sample Preparation for Determination of Crystal Structure and Defect Densities of Nanowires using the Side View

All nanowires discussed in this work were seeded by 30 or 50 nm Au particles and the increase in diameter due to tapering is such that the complete nanowire can be examined using the Philips CM 300 operated at 300 kV. In fact, large portion of the nanowire could even be imaged at high resolution, further assisted by the fact that the edge of the nanowire is thinner than the diameter itself. Hence, no special preparation technique was employed for the side view analysis. Nanowires were dispersed on Cu grids with lacy carbon membranes by gentle contact and swipe with the as-grown sample or sonicate and drop-cast method. The contact and swipe method is fast and easily results in a high density of nanowires on the Cu grid whereas the drop-cast method yields an even distributed population of isolated nanowires and exerts less mechanical stress (by twisting and bending) on the nanowires.

### 3.3.2 Cross-section Sample Preparation of Layers, Planar Nanowires, Nano-Particles Embedded in the Substrate and Nanowires in the Early Stages of Growth using Tripod Polishing

The presence of the underlying substrates is a common feature of all the above stated samples. Hence this needs to be thinned to electron transparency along with the rest of the sample. The main idea of tripod polishing is to create a wedge shape with the sample as shown in Figure 3.8 step (ii), so that the thin edge is thin enough to a level that is electron transparent.

Two pieces of the sample are glued face to face in between another two dummy substrates of the same material and the wedge shape is polished from the two sides of the substrate sandwich consecutively as shown in Figure 3.8 steps (i) and (ii). SiC lapping papers with decreasing roughness are used for this. The micrometers on the tripod are used to control the angle of the wedge and alignment. Once the sample is polished, it is glued to a Cu grid and lifted off in acetone (Figure 3.8 step (iii)).

A final step of ion beam polishing, using a precision ion polishing system (PIPS) is carried out in order to finely thin the edge and remove any damage left on the sample by mechanical polishing. Here, two Ar ion beams with an optimum energy and tilt angles are directed to the thinned area of the sample, so that any undesirable depositions (such as grit) from polishing and amorphised layers are removed. A Gatan PIPS (Model 691) was used to
Ion beam polishing was carried out in two steps. First step was at a higher energy, while the second step, which is intended to remove any re-deposited material from the first stage of ion beam polishing, was done at a lower energy. The ion beam energies used for polishing depends on the sample material and very importantly on the individual sample. Therefore, the progress of polishing had to be carefully monitored and adjusted accordingly. However, the table below provides some typical values used in the ion beam polishing steps of the two materials prepared by tripod polishing in this work.

<table>
<thead>
<tr>
<th></th>
<th>First polish</th>
<th>Second polish</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.5 keV at ± 8°</td>
<td>1.5 keV at ± 8°</td>
</tr>
<tr>
<td>InP</td>
<td>2.8 keV at ± 6°</td>
<td>1-1.5 keV at ± 6°</td>
</tr>
</tbody>
</table>

Table 3.1: Typical ion beam energy values used in the PIPS.
3.3.3 Lateral Cross-Section Preparation of Nanowires using Microtome Sectioning

The nanowires need to be laterally sliced in order to view the growth of radial heterostructures as discussed in Chapters 4 and 7, or to have a clear look at the evolution of cross section shapes along the nanowire as in Chapter 6. As the nanowires are filamental structures, they first need to be reinforced in a resin as shown in Figure 3.9 steps (i) and (ii). Once they are embedded, the substrate is removed by immersing in liquid N\textsubscript{2}, and the resin block with the nanowires is precision sliced using a microtome (Figure 3.9 steps (iii) and (iv)). The slices are usually 30-50 nm thick, and the length-wise region of the nanowire that the slices are collected from can be calculated using this thickness and the approximate number of slices. The microtomed slices that are collected on DI water are then picked up onto lacy carbon grids as shown in Figure 3.9 step (v). The microtomed cross-section samples used for the work presented in this dissertation was prepared in collaboration with Dr. Yanan Guo and Amira Ameruddin.
3.4 Energy Dispersive X-ray Spectroscopy (EDX)

As discussed in Section 3.2, X-rays are one of the types of signals emitted when a high energy beam of electrons interact with the sample. The high energy electrons that hit the sample may eject electrons from the inner shells of the atoms in the sample. Electrons in the outer shells of these atoms which have higher energy, then fall to inner shells to fill the vacancies by emitting photons in the form of X-rays as shown in Figure 3.10 (a). As seen in the same figure, the energy of the X-rays is equal to the energy difference between the two electron shells between which the transition took place. The ability to identify elements using these X-ray signals arise from the fact that each element has a unique atomic structure.

Figure 3.10: (a) Process of X-ray emission when high energy electrons hit the sample. Inset (adapted from [41]) shows the possible sub-levels of electron transitions to K-band. (b) Example of an X-ray spectrum showing different combinations of energies pertaining to different transitions in different elements. (c) An example of a line scan (a closely spaced line of spot scans) taken across an InGaAs quantum well in STEM. Note that the InGaAs material is grown thicker in this case to avoid contribution from the InP barriers. The average relative counts from the mid part of InGaAs shell is used to calculate the composition.
which would give a unique combination of energies in the emitted X-ray spectrum as shown in the inset of Figure 3.10 (a) and 3.10 (b).

Quantitative measurements can be carried out by comparing the relative intensities of the signals. A constant $k_{AB}$, also called the k-factor, is determined, so that the atomic ratio of elements ($C_A/C_B$) can be calculated using the ratio of intensities ($I_A/I_B$) of their respective signals as shown by the equation below.

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$ (3.3)

This is ascertained using a spectrum obtained from a sample with known compositions of A and B. In the case of ternary alloys, two such k-factors are required in order to quantify the composition. For example, composition of InGaAs can be estimated using the k-factors calculated for GaAs and InAs with respect to As. EDX measurement can be carried out both in SEM and TEM systems fitted with EDX detectors. Note that the quantitative measurements in the SEM are slightly more complicated than described above, as the effects of absorption and fluorescence are not negligible due to the sample thickness. The spectra can be obtained from a particular spot on the sample (spot scan), a line of spots (line scan – Figure 3.10 (c)) or in the form of raster scan (EDX maps). TEM should be operating in STEM mode in order to carry out mapping so that the electron beam can raster scan the sample as EDX spectra are gathered at each position. EDX analysis is usually carried out as the last analysis step for a particular sample, due to the high level of damage caused by the electron beam.

In the work presented in this thesis, EDX spot scans in Zeiss Ultra Plus SEM system equipped with an Oxford Instruments 30 mm$^2$ Si(Li) EDX detector have been used to verify the composition of the self-formed droplets in Chapter 5. Line scans taken on nanowire cross-sections using the JEOL 2100F TEM in STEM mode (similar to that shown in Figure 3.10 (c)) have been extensively used in Chapters 4 and 7 in order determine the composition of the InGaAs quantum wells. The same system was used to ascertain the elemental distribution across the nanowire cross-section by EDX mapping as shown in Figure 4.1 (c). The EDX analysis presented in this work was performed in collaboration with Amira Ameruddin and Dr. Yanan Guo.

### 3.5 X-ray Diffraction (XRD)

XRD is another technique where the diffraction of waves by the crystal planes is used to gain information on the crystal structure, similar to diffraction in TEM discussed above. The difference here is that X-rays are used instead of electrons and a reflection geometry is generally used instead of transmission.
Figure 3.11: (a) Satisfaction of the Bragg’s law in an XRD set-up. (b) Bragg reflections in reciprocal space showing symmetric and asymmetric scans and the concept of RSMs. (c) Some changes seen in the symmetric and asymmetric diffraction spots with those in the crystal.

As shown in Figure 3.11(a), constructive interference only takes place when the Bragg’s law of \( n\lambda = 2d_{\text{hkl}}\sin\theta \) is satisfied. As the wavelength of the X-rays \( \lambda \) is constant, \( \theta \) is varied in order to find the diffraction peak a certain set of planes produce. These \( \omega-2\theta \) scans are taken at very high angular resolution targeting one or one set of peaks as indicated in Figure 3.11 (b). Planes that are parallel or tilted with respect to the sample surface can be examined. These scans are called symmetric and asymmetric scans, respectively. Asymmetric scans can give additional information about strain, composition and their gradients, mosaicity and some defects that cannot be distinguished solely from the symmetric scans. Some of these are depicted in Figure 3.11 (c). As seen in Figure 3.11 (c)i, if the layer is strained, substrate and layer peaks may not be able to be collected in one scan and features such as elongation of peaks arising due to the above discussed factors cannot be seen in such a single scan. Therefore scan maps, mostly in reciprocal space are commonly taken (reciprocal space maps - RSMs), by taking multiple scans within a range of \( \omega \) values.
XRD has been used in Chapter 5 in order to characterise the InP layer grown on Si (111) substrates. A symmetric (111) scan and an asymmetric (115) RSM taken using a PANanalytical X’Pert PRO X-ray diffractometer has been used to study the strain and its distribution.

3.6 Atomic Force Microscope (AFM)

SEM provides 2-dimensional images with grey-scale contrast as discussed previously. Yet, it is hard to extract 3-dimensional information such as surface roughness and subtle feature height variations using these SEM images. Hence AFM is commonly used to extract quantitative information on surfaces at the nano-scale.

The AFM consists of a cantilever with a very sharp tip (with radius of curvature in the range of few nanometres) that touches or ‘feels’ the surface of the sample. As shown in Figure 3.12 (a), the deflections of the cantilever (that depends on the variations of the surface) are detected by a position sensitive quadrant photo detector with the aid of a laser beam that is pointed on to the cantilever. The tip scans the sample in a raster pattern and high resolution (sub-nanometre) 3D surface topology information of an entire area can be collected this way. AFMs can operate in three modes. Contact mode, where the tip is ‘dragged’ along the surface, tapping mode, where the cantilever is oscillated at resonance frequency and non-contact mode which is mostly used for measurements involving liquid surfaces such as surface tension measurements. In the tapping mode, the changes in
amplitude of oscillation caused by the interaction forces between the sample and the tip, that in turn depends on the distance is used to measure the surface topology.

In this work, AFM has been used in tapping mode in order to calculate the surface roughness of the InP layers grown on Si substrates in Chapter 5. A Veeco Nanoscope IIIa Multimode AFM, along with BudgetSensors silicon probes was used for this purpose.

### 3.7 Photoluminescence (PL) Spectroscopy

When photons with energy higher than the band-gap is incident on a semiconducting material, the electrons in the valence band of the material may absorb the energy provided by the source and promote to an excited state. This leaves holes in the valence band as shown in Figure 3.13 (a). The electrons then almost immediately relax to the conduction band, mostly by non-radiative recombination. They eventually recombine with the holes in the valence

Figure 3.13: (a) Process of photon absorption and PL emission. (b) Schematic of the PL system set-up.
band by emitting excess energy as photon as shown in the same figure. This process is more straightforward and efficient in direct band-gap semiconductors as discussed in Chapter 2.6. These emitted photons combined with other information and analysis, can be used to determine electron energy levels, impurities, polarisation of emission and carrier life-times. PL spectroscopy is a very powerful and popular technique which is in most cases contact free, non-destructive and quick.

PL is usually excited by a laser with higher energy than the band-gap of the material being analysed. This laser is passed through filters and lenses, and is directed by mirrors to the sample. Similarly the emitted luminescence is directed to a detector via a spectrometer or a monochromator. In most nanowire related measurements, a set up called a ‘micro-PL’ is used. Here, the laser is focused to fine spot using an optical microscope. The emission is collected though the same microscope. The focusing of the laser to a small spot in the range of few square micrometers enhances the spatial resolution, allowing measurements to be carried out on single nanowires.

All PL measurements presented in this work were carried out within micro-PL set-ups. The nanowires were transferred to Si or sapphire substrates in order to avoid emission from the growth substrates, parasitic layers or buffer layers before measurements. For nanowire ensemble measurements, the transfer was done by gently rubbing the two surfaces, whereas for single nanowire measurements, they were sonicated in ethanol before being drop-cast on to the foreign substrate. The drop-cast method was used for the single nanowire measurement due to ease of obtaining well separated individual nanowires using this method.

Figure 3.13 (b) shows the PL set-up within the Horiba Jobin Yvon T64000 micro-Raman/PL system used for PL spectra discussed in Chapters 4, 5 and 7. PL was excited using a HeNe 633 nm or 532 nm DPSS (Diode-pumped solid-state) continuous wave laser. A Si CCD (charge coupled device – 2D array) was used for the spectra in Chapter 5, whereas an InGaAs detector (1D array) was used for the measurements beyond 1000 nm in Chapters 4 and 7. The detectors were cooled with liquid nitrogen in both cases. For low temperature measurements (shown in Chapters 4 and 7), the samples were placed in a continuous flow liquid nitrogen cryostat fitted with the appropriate temperature and flow controllers, which cooled the sample down to 77 K. The PL maps similar to that shown in Figure 4.2 (b) were obtained by acquiring individual PL spectra every 300 nm along the length of the nanowire, using a finely controlled X-Y translation stage. PL mapping was carried out at the Department of Physics at Sapienza Università di Roma by Davide Tadeschi, Dr. Marta De Luca and Prof. Antonio Polimeni, using a system fundamentally similar to the one discussed above.
3.8 Summary

This chapter introduced some of the basics related to nanowire growth, characterisation and sample preparation techniques used in the work presented in this dissertation. The operating principles of some of the equipment, details of experimental set-ups and some of the parameter values used were also discussed.

3.9 References


InP-In\(_x\)Ga\(_{1-x}\)As Core-Multi-Shell Nanowire Quantum Wells Emitting in the 1.3 \(\mu\)m Wavelength Range

**Overview:** This chapter investigates a popular material combination used in planar InP-based devices in the nanowire form. Despite a number of advantages, surprisingly, the InP-InGaAs material combination has not been demonstrated in nanowire-based quantum structures. As InP-InGaAs heterostructures are mostly used in telecommunications devices, radial quantum wells emitting in the short and mid-distance optical communication wavelength range are grown and characterised in order to demonstrate the viability of InP-InGaAs heterostructures in nanowire form. Multiple quantum wells are presented, further affirming the suitability of the InP-InGaAs material system for advanced nanowire device structures.

### 4.1 Introduction

InP-InGaAs material system is being extensively used in planar optical and electronic devices. There are a number of reasons for the widespread use of this material combination. The ability to achieve lattice matching to InP at the composition of 53% In in InGaAs allows the design of heterostructures minimising mechanical strain and critical layer thickness limitation. The possibility to selectively etch one material over the other in a very controlled manner provides a high level of freedom in processing and device fabrication [1, 2]. It has also been shown that the low electron effective mass in InGaAs and the large \(\Gamma\)-\(L\) energy spacing of the binary InP lead to high quantum efficiency and responsivity in devices based on quantum well (QW) structures such as infra-red photodetectors, compared to the other popular lattice matched AlGaAs-GaAs alternative [3, 4]. Most importantly, using this material combination, quantum confined structures such as QWs and dots can be designed and tuned to operate in the 1.3–1.55 \(\mu\)m range[5], which is the low dispersion and low attenuation wavelength region used in modern optical communication systems [6, 7]. InP-InGaAs multiple quantum well (MQW) modulators [7, 8], laser diodes [9, 10], waveguides
and photodetectors [12, 13] are some of such essential components in these communication systems.

Over the past decade, extensive research has been carried out to replicate planar device structures in the nanowire form, with the intention of making use of the inherent advantages of the nanowire geometry in order to improve their performance. Although nanowire heterostructures combining various materials have been extensively reported [14-23], reports of InP-InGaAs material system has been surprisingly rare [17, 24-26]. In fact, InP-InGaAs nanowire QWs have not been reported despite popularity of their planar counterpart.

Core-shell QWs formed on the nanowire side facets are one of the most effective architectures to make use of the large surface area of the nanowires, creating large active regions without compromising the device footprint. Hence, the present study investigates the use of mature InP-InGaAs material system in core-shell nanowire QW structures. The In$_x$Ga$_{1-x}$As QWs are grown around InP nanowires and another InP shell is used as the second barrier. Detail structural analysis is carried out on the nanowire QWs using X-TEM. Photoluminescence (PL) measurements show bright and efficient emission from these QWs with no InP (barriers) emission visible at room temperature. PL mapping carried out along the nanowire is used together with the knowledge gained from structural characterisation in order to ascertain possible sources of the observed broad PL. The QW emission is tuned in the optical communications wavelength region of 1.3 μm by varying the well thickness as well as composition. The WZ phase QWs are modelled using the experimental emission wavelength data and 8-band k-p model. Finally, MQWs comprised of three QWs are grown demonstrating increased emission intensity and the extendibility of InP-InGaAs radial QWs in order to achieve more advanced structures required for device applications such as nanowire lasers [15].

4.2 Experimental Methods

The InP nanowire cores were seeded by 50 nm colloidal Au particles. The Au particle deposited InP (111)B substrates were heated to the growth temperature of 450°C. Substrates were not annealed prior to growth, but TMIn was pre-flown for 15 s before initiating the growth. This pre-flow step greatly reduces the non-vertical nanowire growths that arise from lack of alloying when the pre-growth annealing step is avoided. The TMIn and PH$_3$ flows were $1.62 \times 10^{-5}$ and $5 \times 10^{-3}$ mol/min, respectively. Nanowire core growth was carried out for 30 min at 100 mbar reactor pressure.

After the core growth, the temperature was ramped up to the shell growth temperature of 550°C and the reactor pressure was ramped to 180 mbar which was the pressure normally
used in this MOVPE system for InP-related vapour-solid (VS) epitaxial growth. The nanowire core was annealed for 3 min before depositing a thin InP buffer layer on the nanowire side facets in order to ensure a high quality surface for the subsequent QW growth. After a growth interruption of 5 s the QW growth was initiated. The TMIn, TMGa and AsH₃ flows used for the study of the effect of QW thickness variation were 6.75 × 10⁻⁶, 5.51 × 10⁻⁶ and 1.34 × 10⁻³ mol/min, respectively, giving a vapour phase In molar fraction Xᵥ = [TMIn]/([TMIn]+[TMGa]) of 0.55. The QW growth time was varied between 20 to 180 s depending on the targeted QW thickness. For the study of QW composition variation, the TMIn flow was kept constant at 6.75 × 10⁻⁶ mol/min while varying the TMGa flow to achieve compositions between GaAs and InAs, except in the case of GaAs, where the TMIn source was turned off. The growth time of these composition-varied QWs were also scaled accordingly in order to achieve a nominal thickness of 7 nm. Another 5 s growth interruption was included after the QW growth with AsH₃ left on in order to prevent As desorption from the thin QW [27]. Lastly, an InP barrier shell was grown for 12 min. For the growth of MQW structure, the QW, interruption and barrier growth steps were repeated an additional 2 times. The nanowire single quantum well (SQW) grown with the composition Xᵥ = 0.55 and nominal thickness of 7 nm was used as the principal sample for detailed structural and optical analysis in Section 4.3.

The as-grown nanowires were transferred to sapphire substrates before PL measurements in order to eliminate contribution from the parasitic planar QW that may have simultaneously grown on the substrate. PL was excited using 633 nm continuous wave HeNe laser with a spot size of ~1 μm² and excitation power of 20 μW. PL was detected using a nitrogen cooled InGaAs detector. For the PL mapping study, the nanowires were first spread on a sapphire substrate and then suitable single nanowires were identified by SEM, prior to PL measurements. Spectra were obtained by scanning in 300 nm steps along the nanowires at 80 K. The exciting laser wavelength was 532 nm and spot size was less than 1 μm². The luminescence was spectrally dispersed by a 0.75 m long monochromator equipped with a 300 groove/mm diffraction grating. The signal was detected by a liquid nitrogen-cooled InGaAs array. The PL mapping study was carried out at the Department of Physics at Sapienza Università di Roma. All optical measurements presented in this chapter were carried out on single nanowires. Multiple nanowires were measured from each sample and the exact number of nanowires measured is given under the relevant section.

4.3 Single Quantum Well Nanowires

Figure 4.1 (a) shows an SEM image of the principal sample with nominally 7 nm QW of composition Xᵥ = 0.55 and the inset shows the top view with respect to the cleavage edge. The final structure is around 4.2 μm in length and has a predominantly wurtzite (WZ) crystal
InP-InGaAs Core-Multi-Shell Nanowire Quantum Wells Emitting in the 1.3 μm Wavelength Range

Figure 4.1: Structural characterisation of nominally 7 nm thick In$_{0.6}$Ga$_{0.4}$As QW. (a) 45° tilted SEM view of the QW structure, inset shows a top view of the same sample with respect to the cleavage edge marked in red. (b) Schematic of the nanowire QW indicating the {1-100} side facets. (c) i.-iv. elemental EDX maps of P, As, In and Ga, respectively. v. Over lay of all elemental maps shown (c)i to iv. (d) i. HAADF image of the same nanowire cross-section shown in (c), (d)ii. The zoomed-in view of the area marked in (d)i. indicating the area used for the integrated intensity plot shown in (d)iii. and (d)iv. Calculation of the direct and inverted interface sharpness using the derivative of the integrated intensity.

phase with stacking faults and occasional thin zincblende (ZB) insertions. The InP nanowire core (not shown) is of hexagonal cross-section shape with non-polar {1-100} type side facets. As confirmed by the top view, these {1-100} facets remain unchanged during temperature ramp up or QW growth.

Cross-sections of the nanowire QWs were analysed in order to gain further understanding of their internal structure. The cross-section transmission electron microscopy (X-TEM) samples were prepared by microtome sectioning as described in Chapter 3.3.3. All cross–sections analysed were from the 1-2 μm region from the bottom of the nanowires. Figure 4.1 (c)i-iv are energy dispersive x-ray (EDX) analysis maps from a cross-section of a nanowire from the nominally 7 nm QW sample showing the distribution of each element.
The presence or absence of each element is clear and is as expected, demonstrating the formation of InGaAs QW and InP outer barrier on the facets of the InP nanowire core. Quantitative EDX analysis was carried out on the nanowire cross-sections in order to ascertain the real In$_{x}$Ga$_{1-x}$As composition in the solid phase ($X_s$). Due to limited resolution of the probe size and to avoid contribution from the InP core and barrier, a thicker InGaAs shell grown under the same conditions was analysed for this purpose. The In fraction in solid $X_s$ was found to be $0.600 \pm 0.025$ creating a small lattice mismatch of 0.47% with InP. It should also be noted that alloy segregation seen in the apices and facets of some ternary nanowire structures [14, 17, 19-21, 28] was not observed in this case (at the current InGaAs composition), within the sensitivity of the measurements.

Figure 4.1 (d) shows a high-angle annular dark field (HAADF) STEM image of the same cross-section as in Figure 4.1 (c). The QW is visible in lighter contrast compared to the InP core and barrier. The magnified view from the marked area shown in Figure 4.1 (d)ii reveals that the first InP to InGaAs (direct) interface is sharp while the second InGaAs-InP (inverted) interface is diffused compared to the first. As shown in Figure 4.1 (d)iii, this can be further confirmed by the rate of change (derivative) of the integrated intensity profile taken from the area marked in yellow in Figure 4.1 (d)ii, where it is clearly seen that the FWHM (marked with black arrows) is larger for the inverted interface. Similar difference in sharpness has also been observed in InGaAs-InP QWs grown on planar surfaces [29-32]. The same causes are applicable to QWs grown around nanowires as the growth mechanism is similar (VS) in both cases. One main cause is group V interdiffusion [30, 33-35] that takes place as a result of As-P exchange which is promoted by the stronger chemical bond between Ga and P [30] as well as the As carryover effect [33-35], resulting in higher level of interdiffusion at the inverted interface. Interdiffusion could also take place in the group III sublattice [27, 35-37]. Yet, this is known to be lower than that of group V [35-37], and in the present case it would be extremely low due to the low growth temperature [38]. Furthermore, group III interdiffusion would be energetically unfavourable as it would increase the lattice mismatch leading to increased compressive strain in the QW. More importantly, surface undulations and roughening that takes place during the InGaAs growth and the subsequent growth interruption (before the second barrier growth) lead to the formation of the more diffused inverted (second) interface as seen here [29, 31, 32]. This roughening effect could also be enhanced by the 0.47% lattice-mismatch [31].

Figure 4.2 (a) shows representative PL spectra taken from a single nanowire QW at room temperature and 77 K from the principal sample discussed in Figure 4.1. The laser spot was focused on the middle of the nanowire for the measurements shown in Figure 4.2 (a). Note that the two spectra may not be from the same nanowire. The nanowire QWs show bright emission with a clear single peak at room temperature as well as 77 K. It should be noted that the ripples observed in the 1300 – 1400 nm range are due to system response and
Figure 4.2: Optical characterisation of single QWs. (a) Representative room temperature and low temperature spectra from a single QW nanowire, insets (i) and (ii) zoom in to the 800-1000 nm wavelength region of the 77 K and 300 K spectra, respectively, where the InP emission is expected. (b) PL map of a single nanowire taken at 80 K, inset shows the SEM image of the nanowire scaled and rotated to align the map.

water vapour absorption. The two insets in Figure 4.2 (a)i. and ii. are the magnified plots showing the 800 – 1000 nm wavelength range. It can be seen that no emission from the InP nanowire core or barrier is visible at 300 K, whereas a very weak signal is observed at 77 K. This shows that the quantum well is highly efficient in capturing carriers, almost completely avoiding recombination in the InP core or outer barrier. This is one of the main differences seen in the current material system compared to the more commonly reported GaAs-AlGaAs nanowire QWs, where emission by the nanowire core is almost always visible and in most
§ 4.3 Single Quantum Well Nanowires

cases stronger than the GaAs QW emission [39-41]. The reason for this is the presence of bulk-like GaAs nanowire core, which has the lowest energy gap in the structure. Hence, the carriers excited in or close to this region are more likely to recombine in the GaAs nanowire core rather than at the QW. Whereas in InP-InGaAs nanowire QWs, the QW has a lower energy gap than the InP core, making it the preferable recombination location in the entire structure.

However, the PL peaks are somewhat broad here. The average FWHM is around 175 nm (110 meV) at room temperature and 137 nm (102 meV) at 77 K. Linewidth-broadening is commonly observed in ternary planar QWs due to alloy disorder in the lattice [42, 43]. Interface diffusion is another cause that results in broader emission peaks [44, 45]. In addition to these, in the case of nanowires, inhomogeneities can exist in a much longer range due to the nanowire geometry and shell growth mechanism. In planar QW growth, the adatoms are directly adsorbed on the growth surface and diffusion takes place two dimensionally on the same surface; whereas in nanowires, in addition to adsorption directly on the side walls, the adatoms could also be adsorbed on the substrate surface and then diffuse towards the side walls of the nanowire. Hence, when a ternary alloy is grown, the species with higher mobility could diffuse further towards the top region of the nanowire compared to the one with lower mobility. Therefore, in the case of InGaAs, the QW ‘tube’ could be slightly richer in In towards the top of the nanowire causing a composition inhomogeneity in a much longer range than by alloy disordering discussed above [46]. This could result in an overall broad peak in the single nanowire measurements [16]. Similarly, the aforementioned diffusion from the substrate could lead to a variation in QW thickness along the length of the nanowire leading to a broad peak [46, 47].

PL mapping was carried out along the nanowires in order to determine the spatial origin of the emission and hence if the broad PL is a result of such variations along the nanowire. Eight such maps were examined and Figure 4.2 (b) shows a PL map from a representative nanowire with the SEM image of the same nanowire placed relative to the scan direction and y-axis of the map. The first main observation is that bright emission can be observed from a large region of the nanowire containing the QW, which shows that the QW growth has taken place around the whole nanowire core. Note that the length of the InP nanowire core is 3.6 μm, which would be the active region containing the QW. The top ~600 nm of the nanowire (marked by a red dashed line in Figure 4.2 (b)) has grown during the InP outer barrier growth and would not contain the QW. The second observation is that there is no, or very little (< 18 nm) shift in emission peak along the length of the nanowire in all the nanowires measured. It could also be seen that the broadness of the peak is present along the complete length of the nanowire. These results indicate that the broad peak observed in the spectra is not due to the above discussed compositional or thickness variations along the length of the nanowire.
Hence, the source of the broad peak should be more local in nature and common to the entire length of the nanowire as suggested by the homogenous emission. With the knowledge of the structural properties discussed in the previous section, three such causes can be identified. First is the interface diffusion (and alloy disordering) which was discussed above [42, 43, 48, 49]. This is the most likely cause also considering the current alloy composition of InGaAs [48, 49]. Secondly, in this case, uneven growths at stacking faults [50-53] could cause monolayer fluctuations in the QW thickness. Peak broadening due to similar growth variations has been observed before [53], although sharp peaks like those seen in ref [53] is not apparent in the current spectra. Due to uniformly distributed high density of stacking faults along the whole nanowire (Figure 4.3 (b)), this effect could very well be contributing to the homogenous broad PL emission observed along the entire length of the nanowire, not only due to monolayer fluctuations in thickness, but also due to band structure variation between WZ segments and stacking faults (which could behave like ultra-thin ZB segments) [54, 55]. The third possibility could be the slight difference in QW thicknesses on different facets that is seen by X-TEM. This could be caused by effects such as different levels of shadowing by the randomly placed neighbouring nanowires during growth [56, 57].

**Figure 4.3:** Stacking fault distribution along the nanowire. (a) Low magnification TEM images showing the QW and the area used for the high magnification image. (b) High magnification TEM image showing the rather even distribution of stacking faults (indicated by red arrows). The black thick arrow indicates a ZB insert. All images are taken along <11-20> zone axis.
§ 4.4 Tunability of Nanowire Single Quantum Wells

4.4.1 Tunability by Variation of Quantum Well Thickness

As mentioned in Section 4.1, one main advantage of the InP-InGaAs material combination is the possibility of avoiding lattice mismatch. When the InxGa1-xAs composition is selected to be x=0.53, heterostructures can be grown without critical thickness limitations and dislocation generation due to lattice mismatch [58]. In the case of QWs, this gives the opportunity to tune the QW emission almost in the complete wavelength range from bulk InP to bulk In0.53Ga0.47As value without concerns on degradation of crystal quality, by changing the well thickness.

Here, the thickness of In0.6Ga0.4As QWs is tuned in the 1.3 μm wavelength region. This composition is close to the lattice matched composition with InP with only 0.47% mismatch. The well thickness was varied simply by changing the growth time from 20 to 180 s. The corresponding expected nominal thicknesses (calculated from available empirical data for growth on InP (100)) for these growth durations were 2 to 18 nm. Note that, even though no quantum confinement is expected at larger thicknesses, the 180 s QW growth was carried out for the completeness of the growth rate study. The actual average thicknesses of the QWs were measured using high resolution (HR) TEM images of the nanowire cross-sections and are plotted against the growth time and nominal thickness in Figure 4.4 (a). The QW thickness was measured using the derivative of the integrated intensity along the well as shown in Figure 4.4 (b) in order to avoid ambiguity related to the diffused interfaces. QWs on the facets of at least five nanowires were measured for each data point. The error bars indicate the standard deviation of the measurements. The WZ QW growth rate on the nanowire facets is generally lower than nominal values expected from the empirical data for InGaAs growth on ZB InP (100) substrates, except in the case of very thin 2 nm QW.

This considerable difference is due to two reasons. First, the equivalent facet orientation of nanowires in the ZB phase itself is different from (100), and they generally grow slower than (100) facets under the considered growth conditions (for example {110} and {112} facets) [59] [60]. Second, the growth rate of the side facets of nanowires in WZ phase is inherently even lower than their ZB equivalent [51, 52], making the actual thickness much lower than expected. The initial fast growth of the QWs up to about 2 nm in thickness seen in Figure 4.4 (a) could be due to the faster growth rate of InGaAs on InP compared to homoepitaxial growth on InGaAs, which takes place once the InP nanowire core is sufficiently covered by the initial InGaAs layers. The initial apparent increase in thickness could also be an effect of the As-P exchange that was discussed earlier. However, the growth rate of the QWs seems to remain constant once the well thickness is over ~2 nm, showing a linear relationship for QW thickness with growth time. This relationship between growth
time and QW thickness, in conjunction with information given in Figure 4.4 (d) becomes useful in estimating growth times in order to grow QWs with the required emission wavelengths.

Figure 4.4 (c) shows the monotonic shift in the emission wavelength with QW thickness in the 1.3 μm wavelength region. Figure 4.4 (d) plots the emission wavelength against actual QW thickness measured in Figure 4.4 (a). Error bars indicate the standard deviation of the emission wavelength measurements. Emission from at least seven nanowires was measured for each thickness.

Figure 4.4: Tunability of QW emission by varying thickness. (a) Actual thickness variation with the nominal thickness and growth time. (b) Calculation of actual QW thickness using the HR-TEM images. (c) Monotonic shift in the emission wavelength with the QW thickness. (d) Experimental and calculated emission wavelengths with and without bowing parameter fitting for varied QW thicknesses. All error bars represent the standard deviation of the measurements.
The expected ground state emission wavelengths for In$_{0.6}$Ga$_{0.4}$As QWs with thicknesses in the experimentally examined range were calculated using the 8×8 k-p model. The calculations were carried out for WZ m-plane (the {1-100} family of planes – same as the facets of the nanowires) using the nextnano© simulation software [61]. Some of the key parameters used to create WZ phase InP and InGaAs materials are given in Tables 4.1. Arsenide and phosphide WZ materials are not available naturally in bulk form and hence it is not possible to find all material parameter values required for QW emission calculation in the literature. Therefore ZB values and realistic estimations are often used in most WZ calculations [23, 53]. Here too, the same approach is adopted where appropriate. The blue curve in Figure 4.4 (d) is the calculated curve considering linear interpolation between GaAs and InAs to derive material parameters of In$_{0.6}$Ga$_{0.4}$As, as values of bowing parameters of WZ InGaAs are also not available in literature. The curve does not fit the experimental values, possibly due to a number of reasons (as discussed later), of which ignorance of bowing parameters could certainly be one. Here, the bowing parameter of In$_x$Ga$_{1-x}$As band-gap, which is one of the key parameters that is directly affecting the calculation, is used as the fit parameter in order to fit the above blue curve to the experimental data. A close fit can be obtained with a bowing parameter of 0.12 eV as shown by the red curve. Indeed, other parameters or even a combination of fitting parameters could have been used for the fitting, as normally done when one or more parameters are unknown similar to the current case [53, 62, 63]. However, here, a single parameter was used for simplicity. The derived energy-gap bowing parameter value of 0.12 eV can be deemed reasonable compared with the known values of other materials like ZB InGaAs and WZ InGaN [64, 65].

There are number of aspects that have not been or cannot be considered in the theoretical simulations. As mentioned above, bowing parameters of WZ phase InGaAs is unknown. Some of the values used, for example the effective electron masses are theoretical or based on ZB values, which could be different experimentally in the WZ phase. Moreover, even the experimentally determined values such as band-gaps of GaAs and InAs are also still under debate. There are also aspects such as strain relaxation which could be taking place, especially in the thicker QWs, where the current simulation and the experimental value plots also show a higher discrepancy. Yet, it is considered to be coherent and fully strained in the calculations. Another structural observation that is not included in the simulations is the stacking faults and the occasional thin ZB inclusions. These not only lead to complex carrier separation and peak energies but also to charge accumulation due to saw-tooth-like potential build-up due to spontaneous polarisation in WZ regions [66-69] along the nanowire (WZ c-axis). The nanowire QW could also behave differently to the simulated planar QW due to its geometrical tube-like shape. For example it has been shown that ground state carriers can be confined to the apices of the facets [39, 54].
In the next section, emission wavelength tuning in the 1.3 μm region by variation of QW composition is demonstrated.

### 4.4.2 Tunability by Variation of Quantum Well Composition

As shown in previous section, thickness variation for a fixed QW composition is one easy approach to tune the emission wavelength of the QWs, as this could be achieved simply by tuning the growth time once the growth rate trend is identified. Dislocations stemming from lattice mismatch and strain related complications can also be eliminated for all thicknesses by choosing the composition to be lattice matched to InP. However, four drawbacks can be identified in relation to this approach, especially in the achievable high and low wavelength limits. Firstly, the longest wavelength achievable is limited by the bulk band-gap of the chosen QW alloy. Secondly, the sensitivity of the wavelength to thickness reduces for thicker QWs as the emission wavelength reaches the bulk emission wavelength of the QW material. Thirdly, in some cases, although not seen in the current study, relatively higher level of broadening and multiple sharp peaks can be observed for very thin QWs due to higher sensitivity to mono-layer fluctuations and quantum dot like formations [39, 40]. Finally, the electron capture efficiency could also be low for very thin QWs.

**Table 4.1:** WZ InP, GaAs and InAs material parameters used for QW emission wavelength simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>InP</th>
<th>GaAs</th>
<th>InAs</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant along a at 300 K</td>
<td>4.1423 [70]</td>
<td>3.9976 [71]</td>
<td>4.274 [72]</td>
<td>Å</td>
</tr>
<tr>
<td>Lattice constant along c at 300 K</td>
<td>6.8013 [70]</td>
<td>6.5281 [71]</td>
<td>7.025 [72]</td>
<td>Å</td>
</tr>
<tr>
<td>Direct energy gap at 300 K</td>
<td>1.427 [73]</td>
<td>1.437 [74]</td>
<td>0.396 [75]^5</td>
<td>eV</td>
</tr>
<tr>
<td>Varshini coefficient α</td>
<td>4.8 × 10^−4 [76]</td>
<td>5.61 × 10^−4 [77]</td>
<td>2.76 × 10^−4 [78]^6</td>
<td>eVK^−1</td>
</tr>
<tr>
<td>Varshini coefficient β</td>
<td>300.7 [76]</td>
<td>376 [77]</td>
<td>83 [78]^5</td>
<td>K</td>
</tr>
<tr>
<td>Crystal field splitting</td>
<td>0.147 [79]</td>
<td>0.103 [80]^6</td>
<td>0.122 [75]</td>
<td>eV</td>
</tr>
<tr>
<td>Spin orbit splitting</td>
<td>0.084 [79]</td>
<td>0.466 [80]^6</td>
<td>0.41 [75]</td>
<td>eV</td>
</tr>
<tr>
<td>Electron effective mass along a</td>
<td>0.088 [81]</td>
<td>0.082 [81]</td>
<td>0.042 [81]</td>
<td>m_0</td>
</tr>
<tr>
<td>Electron effective mass along c</td>
<td>0.105 [81]</td>
<td>0.090 [81]</td>
<td>0.060 [81]</td>
<td>m_0</td>
</tr>
</tbody>
</table>

^4 Value at 290 K
^5 Assuming ZB Varshini parameters
^6 Assuming same value at room temperature
When the QW structure is comprised of a ternary (or quaternary) material, its emission can be tuned also by varying the composition of the alloy. By using this method, these limitations at very small and large thicknesses can be minimised, albeit at the possible expense of formation of dislocations due to lattice mismatch. However, it should be noted that the possibility of strain relaxation through dislocation formation is slightly less in the case of nanowire radial QWs compared to the planar case as discussed in Chapter 2.5. Hence, in the case of nanowire QWs, the composition range that can be accommodated is slightly larger than its planar counterpart of the same thickness. Also, strain is not always disadvantageous. Strain induced alterations in the electronic bands can be used to achieve different properties such as the lifting of the degeneracy of heavy and light hole valence bands, indirect band-gaps [82] and type II band alignment between the QWs and barriers (as will be discussed later) [83, 84]. It could also improve performance of some devices like in lasers [85].

Here, the composition of the QW is varied from GaAs to InAs. All samples were morphologically similar and Figure 4.5 shows representative spectra from nominally 7 nm GaAs, In0.35Ga0.65As and In0.6Ga0.4As QWs. The spectra show a shift towards higher wavelengths with increasing In composition in the well, as expected. No reliable spectra could be obtained from the QWs with higher In composition and InAs QWs, most probably due to the emission being beyond the wavelength range of the InGaAs detector used, which is 1600 nm. It should also be noted here, that even though the precursor flow rate and the growth time of the QWs were controlled in order to achieve QWs of same thickness, due to the different growth rates of different compositions (alloys containing high percentage of Ga
InP-InGaAs material combination to tune QW emissions in a desired wavelength range (1.3 μm in this case) by composition variation.

One interesting observation is the QW-like behaviour of the GaAs insert. The band-gap of WZ GaAs is very close, but slightly higher than InP with values of 1.437 and 1.427 eV (863 and 869 nm) respectively, as given in Tables 4.1 and 4.2. However, the lattice constant of GaAs on m (or a) planes is 3.5% smaller than InP (see Table 4.1). Hence, GaAs is under tensile strain, which shifts its band-gap (wavelength) below (above) that of InP, thereby forming a QW [83, 86]. It has been shown that the band alignment in ZB InP-GaAs-InP QWs and InP-In_{0.6}Ga_{0.4}As-InP QWs with x ≤ 0.20 is of type II, with holes confined in GaAs or InGaAs layer and electrons confined in InP [84, 87]. This may or may not be the same in the WZ phase as changes in the electronic band structure with the strain is complex [83], and requires further work beyond the scope of this dissertation.

Two approaches of emission wavelength tuning of InP-InGaAs nanowire QWs were presented in this section. Although each has some limitations the two approaches together provides flexibility and control in tuning the emission of InP-InGaAs QWs grown on nanowires demonstrating the appeal of this material combination for nanowire-based optical communication device components.

In the next section, the single QW structure discussed in section 4.3 is further extended to grow multiple quantum wells demonstrating the possibility to grow more complex structures aiming for applications which require more QW active volume, such as lasers, light emitting diodes (LEDs) and photodetectors.

### 4.5 Multiple Quantum Wells

QWs are rarely used as a SQW in most optical communication related devices. Instead, multiple QWs are used [7, 8, 11] due to advantages such as higher efficiency, gain and total power output depending on the application and structure [88-90]. Here, the structure discussed in detail in section 4.3 is extended to grow three nominally 7 nm thick In_{0.6}Ga_{0.4}As QWs separated by InP barriers.
Figure 4.6 (a) shows the room temperature emission from a typical MQW nanowire. Inset shows a low magnification X-TEM image and the corresponding schematic. The emission wavelength of the MQW is $1343 \pm 10$ nm, around 78 nm lower in wavelength than the SQW grown under similar conditions. The small 10 nm standard deviation value of the measurements from the seven MQW nanowires shows that the emission wavelength does not vary much between nanowires. No excess broadening of emission was observed, contrary to the expected broader linewidth due to non-uniformities between the QWs [90, 91]. The intensity of the MQW nanowires is much higher than that of the SQWs in general, with an average value of an order of magnitude higher for the same excitation power as shown in Figure 4.6 (b). However it should be noted that the quantitative values are not completely meaningful in this case, as the variation in intensity across each sample, especially of the MQWs, is very high as seen in Figure 4.6 (b).

The thickness of the QWs in the MQW structure was examined in order to understand the observed blue shift in comparison to the SQW. The average thickness of a QW in the MQW structure was found to be $3.35 \pm 1.29$ nm as opposed to $4.74 \pm 1.01$ nm in the case of

**Figure 4.6:** Optical characterisation of the MQW nanowires. (a) A representative room temperature PL spectrum from a single MQW nanowire, inset shows a X-TEM image with the schematic aligned. (b) Intensity of the PL measured from the SQW and MQW nanowires, red dashed line and black line represent the average values of the SQW and MQW measurements, respectively.
the SQW. According to the curve fitted to the previous experimental data in Figure 4.4 (d), the thickness of 3.35 nm would give an emission wavelength of 1357 nm, which is close to the observed value of 1343 nm. The cause of this discrepancy in the thicknesses is not completely clear at this stage. In contrast to the SQW, two additional InP barriers were grown at 550°C in the case of the MQW, which took 12 min each. This could mimic an annealing effect on the first two (inner) QWs, which could enhance interdiffusion and hence reduce the effective thickness [35, 92]. In addition, if the volume growth of InGaAs is constant, the outer QWs should be getting progressively thinner as the circumference of the nanowire is increasing with the inner QW and InP barrier growths. This would lead to growth of thinner outer QWs as the number of QWs increases. Further experimental work and simulations are required to ascertain the combinational effect of these arguments.

The strong emission from the MQWs emitting in 1.3 μm region demonstrated here, shows the scalability and the ability to extend the InP-InGaAs nanowire QWs to form more advanced structures that form the basis for devices such as lasers and LEDs.

4.6 Summary

In summary, this chapter investigated the popular InP-InGaAs material combination which is commonly used in planar telecommunication related applications, in nanowire form. InGaAs radial QWs were grown on WZ phase InP nanowire cores. The nanowire QWs were found to grow conformally around the nanowire core and showed some similarities to ZB phase planar InP-InGaAs QWs, such as interface diffusion and some dissimilarities such as broader PL. Despite this, optical characterisation revealed bright room temperature PL with efficient carrier capture by the QW. Tunability of the QW emission was demonstrated in the 1.3 μm optical communications wavelength region by varying the QW thickness as well as In\textsubscript{x}Ga\textsubscript{1-x}As composition. The WZ InP-InGaAs QWs were optically modelled using WZ material parameter values and 8×8 k-p approximation. This optical model and the knowledge of the growth rate of the QWs can be used to fine tune growth parameters in order to achieve the required wavelength values. Finally, the SQW structure was extended to grow MQWs, demonstrating the possibility to grow more advanced structures. The results show the suitability of the InP-InGaAs material system for nanowire-based radial heterostructures with tunability, flexibility and scalability.
4.7 References


§ 4.7 References


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InP-In$_{1-x}$Ga$_x$As Core-Multi-Shell Nanowire Quantum Wells Emitting in the 1.3 $\mu$m Wavelength Range


4.7 References


InP-In$_{1-x}$As Core-Multi-Shell Nanowire Quantum Wells Emitting in the 1.3 μm Wavelength Range


InP-In$_{1-x}$As Core-Multi-Shell Nanowire Quantum Wells Emitting in the 1.3 μm Wavelength Range
Chapter 5

High Vertical Yield InP Nanowire Growth on Si (111) Using a Thin Buffer Layer for Integration with Si Technology

Overview: Even though the InP nanowire growth on InP (111) substrates is reasonably well developed by now, future integrated circuits would require the nanowires to be grown on Si substrates so that the nanowire-based optical components can be integrated with Si-based electronics on a single chip. However, growth of Au catalysed nanowires directly on Si would not be an option in reaching this goal, as Au, when in contact with Si would easily diffuse and form detrimental mid-gap electronic states in Si. Therefore, in this chapter, growth of InP nanowires on Si is achieved using an intermediate buffer layer. The buffer layer growth is optimised so that the resulting nanowires grow similarly to those grown on InP substrates while yielding a very high percentage of vertical nanowires.

5.1 Introduction

As discussed in Chapter 1.1, III-V compound semiconductors like InP are far more attractive for optoelectronic and high speed device applications than Si, due to their higher carrier mobility and, direct and tuneable bandgap [1-6]. However, Si is the material of choice for microelectronic devices and will remain so, due to the advantages of low cost, abundance and superior mechanical and thermal properties. Therefore, in order to provide complete functionality to the new generation InP nanowire devices, it is required that InP nanowires can be grown on Si substrates; thus enabling the monolithic integration of these optoelectronic devices with the mainstream Si microelectronic technology [7, 8].

III-V layer growth on Si is complicated by lattice mismatch, thermal expansion coefficient mismatch and polarity related issues [9-11]. In the case of nanowires, the lattice mismatch and thermal expansion coefficient mismatch problems are partially eliminated for smaller particle sizes due to the possibility of strain relaxation at the bottom of the nanowires.
High Vertical Yield InP Nanowire Growth on Si (111) Using a Thin Buffer Layer for Integration with Si Technology

[12, 13] as discussed in detail in Chapter 2.5. However, in addition to polarity, complexities such as the Au catalyst particle diffusion into Si and the rapid formation of the native oxide on Si during sample preparation for nanowires also come into play [14-20] in the case of nanowires. The overall yield and/or vertical yield of nanowires have been rather low for Au catalysed InP nanowires on Si [14, 15, 18, 21-23]. Regardless, direct growth on Si using Au would not be ideal as Au easily diffuses in Si and form mid-gap states degrading electronic device performance [24].

Gao et al. have been successful in achieving nanowires with 100% vertical yield on Si by using the In droplet self-catalysed technique [25]. Yet, in this instance it is still seen that the growth window (in terms of growth parameters) for high vertical yield, is rather restricted; leaving limited room for fine tuning of morphology and crystal quality. This could limit the optical properties and hence the applicability of these nanowires in devices compared to those grown on InP substrates.

On the other hand, homoepitaxially grown InP nanowires have been successfully demonstrated in applications such as high efficiency solar cells and bright single photon emitters [3, 4, 6] (also see Chapter 1.2.1 for more applications). A thin InP buffer layer grown on Si could be able to mimic an InP substrate for the nanowires. As the nanowire will now be grown on an InP layer, there will not be any lattice or thermal expansion co-efficient mismatch irrespective of the particle size. The polarity of the layer defines the polarity of the nanowires, it eliminates the Si oxide related complexities and most importantly, acts as a barrier between the Au particle and the Si substrate. Thus, the buffer layer approach is a promising solution to migrate the above-mentioned applications which are demonstrated on InP substrates, onto Si substrates without changing the properties of the nanowires. In other words, this technique preserves the flexibility of same substrate growth while eliminating the intricacies of direct growth on Si. The thin buffer layer can additionally act as a contact layer or a doped layer to enhance functionality when designing devices [26]. High quality GaAs and InAs nanowires have also been grown on Si using a similar approach [26-29].

This chapter focuses on the growth of InP nanowires on Si (111) substrates using a thin (< 75 nm), InP buffer layer. Since the buffer layer acts as the platform for the epitaxial nanowire growth, it is important that it has a smooth morphology for the nanowires to grow vertically. Due to the 8% lattice mismatch between InP and Si, the epitaxial growth tends to be islanding in nature [30]. Hence a two-step approach is commonly adopted [9, 31]. Here, the first (nucleation) layer is expected to cover the Si substrate as much as possible and a higher quality, smooth second layer, suitable for the nanowire growth is then grown on the first layer. This is achieved by optimising the growth temperature and V/III precursor ratio during the growth. This ‘double’ buffer layer is annealed at high temperature in order to investigate the potential improvement in the crystal quality [10]. InP nanowires are then
grown on the buffer layer using the same procedure as homoepitaxial growth on InP substrates [32]. The buffer layers and nanowires are characterised using a number of techniques and the nanowires grown on the buffer layers are compared with those grown directly on InP substrates.

§ 5.2 Experimental Methods

The native oxide on on-axis Si (111) substrates was removed by immersing them in 4.4% HF solution for 2 min. The samples were then rinsed with de-ionised water and immediately transferred to the MOVPE reactor to prevent re-oxidation. Samples were annealed at 750°C for 10 min under H2 to desorb potential surface contaminants. After annealing, the samples were cooled to the initial layer growth temperatures between 350 and 450°C. Once the growth temperature was reached, TMI and PH3 were turned on simultaneously to initiate the first layer growth. TMI flow rate was fixed at $6.70 \times 10^{-6}$ mol/min while PH3 flow was varied in order to achieve V/III ratios between 200 and 3330. After 10 min of first layer growth, the temperature was ramped up to between 550 – 680°C under PH3 flow for the second layer growth. For the second layer, TMI flow was the same as in the initial layer growth and PH3 flow was varied to achieve V/III ratios between 67 and 1000. Growth time was 20 min. At the end of this step, the samples were cooled under PH3 flow to prevent decomposition of the InP layer. For another batch of samples, an additional annealing step was carried out in situ for 30 min at 700°C under PH3 flow.

The samples were then unloaded from the reactor and 30 nm diameter Au particles were dispersed on them. Nanowires were also grown on InP (111)A, (111)B and bare Si (111) substrates for comparison. The sample preparation process for buffer layers and InP substrates was same as that described in Chapter 3.1.3. In the case of bare Si substrates, an additional etching step was carried out for 2 min in 4.4% HF immediately prior to the above standard treatment. The treated samples were then loaded into the reactor and annealed at 600°C for 10 min under PH3 flow before nanowire growth. Nanowires were grown for 20 min at 420°C, with TMI and PH3 flows of $1.21 \times 10^{-5}$ and $4.24 \times 10^{-3}$ mol/min, respectively.

The morphology of growths was studied by SEM and EDX measurements were also carried out within the same system with an operating voltage of 8 kV. The surface of the buffer layers was studied by AFM while TEM and XRD were used for the study of the crystal structure. The nanowires were transferred from the as-grown substrates to bare Si substrates by gently rubbing the two surfaces before PL analysis in order to avoid emission from the buffer layer. TEM cross section samples of the buffer layers were prepared by mechanical tripod polishing. Polarity of the layers were verified by etching in a 0.1% Br2:methanol solution.
5.3 Buffer Layer

5.3.1 Initial Layer Growth

Two step layer growth is used as an effective way to achieve smooth and high crystal quality III-V layers on lattice mismatched Si [9, 31, 33]. The growth mechanism on highly lattice mismatched substrates usually results in formation of islands. Hence full Si substrate coverage is achieved by a high density of closely nucleated small islands. In order to realise this, a relatively low growth temperature is used for the initial layer. Figures 5.1 (a-d) illustrate the morphology of the initial layers grown at temperatures between 350 and 450°C with a V/III ratio of 3330. As it can be clearly seen at 450°C, sparse and large islands are formed. At high growth temperatures, the surface diffusion length of In adatoms is larger, allowing them to migrate to an already nucleated site, thereby expanding the sparse and large island structures. Island size becomes smaller with decreasing temperature and full coverage of the Si surface is achieved at temperatures of 375 and 350°C. At lower temperatures, the mobility or the diffusion length of In adatoms is much reduced, which forces the formation of smaller islands close to each other. These temperatures are lower than the temperature used for the initial layer growth of GaAs on Si substrates by Kang et al. [27] due to the larger lattice mismatch between InP and Si and the larger diffusion length of In compared to Ga under similar conditions [34, 35].

However, it should be noted that the lowest temperature studied here (350°C) is also not suitable due to the presence of non-epitaxial self-seeded growths (marked with arrows in Figure 5.1 (a)) that take place on the underlying layer. EDX measurements confirm that these self-seeded growths arise from In droplets. Their formation can be explained by considering the decomposition temperatures of the two precursors used. TMIn and PH3.

Figure 5.1: SEM images of the initial layer grown at different temperatures as indicated. V/III ratio was kept constant at 3330. Scale bar is 1 μm in the main images and the same scale bar is 200 nm in the insets of (b) and (c).
decompose between 300-380°C and 400-575°C respectively, under conditions comparable to those used in this study [36, 37]. The presence of PH₃ further lowers the decomposition temperature of TMIn by about 50°C, whereas the effect of TMIn in reducing PH₃ decomposition temperature is negligible at the V/III ratios used here [37]. Therefore at 350°C, TMIn is almost fully decomposed whereas PH₃ is barely starting to decompose. Under such conditions, the excess In form droplets on the surface and they eventually catalyse InP whiskers grown through the vapour-liquid-solid (VLS) mechanism.

A similar In droplet formation can be observed for the initial layers grown with lower V/III ratios, where the PH₃ flow was reduced while keeping the TMIn flow constant. Figures 5.2 (a-c) show the layers grown at different V/III ratios at a constant growth temperature of 375°C. Due to the aforementioned decomposition temperature difference, the real V/III ratio during growth is much smaller than the nominal V/III value at the low growth temperature of 375°C. When the supply of P atoms is low, excess In starts to form into droplets. A very high nominal V/III ratio of over 3000 is necessary to prevent droplet formation at this temperature. The average droplet size is slightly larger in the V/III=200 growth compared to V/III=1000 growth, and many smaller droplets can be seen in the latter. Due to the rougher surface of the layer grown with V/III=1000, the diffusion of In adatoms as well as the mobility of smaller In droplets is inhibited, hence the Ostwald-ripening process is limited in the V/III=1000 growth preventing the formation of larger In droplets.

In order to grow a thin, smooth, high quality second layer, the initial nucleation layer should fully cover the Si substrate and be as smooth as possible so that smooth morphology of the second layer can be achieved with minimal thickness. For these reasons, the initial layer grown at 375°C temperature and V/III ratio of 3330 is selected for the growth of the subsequent layer.
5.3.2 Second Layer Growth

As the Si substrate is covered with small islands that can provide the nucleation sites for the subsequent growth, the second layer can be grown at a high temperature to ensure better crystal quality. This layer nucleates as smooth triangular terraces on the initial layer. These terraces then merge laterally with further deposition of material and cover the initial rough layer. Figures 5.3 (a-d) show the SEM images of the second layer grown at temperatures between 550 and 680°C with a constant V/III ratio of 1000 and Figures 5.3 (e-g) show the effect of V/III ratio at a fixed growth temperature of 600°C. At high temperature (680°C), 3-dimensional growth is dominant, resulting in the formation of pyramid-like structures rather than terraces. When the growth temperature is too low (550°C), the morphology degrades such that a rough surface, more similar to the initial islands rather than the terrace structure is observed. This temperature dependent behaviour can also be attributed to the surface diffusion of the adatoms. When the growth temperature is high, adatoms can migrate to an energetically favourable site in the underlying dislocation network [11, 38], which would be a newly nucleated relaxed terrace at an unstrained location of the initial layer [39]. Continued growth on the facets of these terraces leads to the pyramid-like structures. When the growth temperature is too low (550°C), adatom mobility is also low, which leads to preferential adatom attachment to the existing initial layer and continuation of island growth similar to the initial layer. As the morphology is rough in this layer, a much thicker layer has to be grown before the surface smoothens. In addition, this layer is more defective as the defects in the low temperature grown initial layer can more easily propagate to the second layer, when the growth is a continuation of the initial layer compared to a freshly nucleated second layer. At an intermediate temperature of 600°C, a smooth layer is obtained. Note that there are a few high terraces above the average layer height appearing intermittently as seen in Figure 5.3 (b). These are reported to be terraces bordered by stacking faults inclined to the substrate surface [9], which evidently (Figures 5.4 (b) and (c)) have originated in the initial layer and continued through the second layer. However, these high terraces are not found to cause a problem during nanowire growth as the terrace tops are largely flat compared to the size of the Au particles used for nanowire growth.

Higher V/III ratios are known to promote 2D layer growth over 3D island growth [40] and the same effect is observed here. As shown in Figures 5.3 (e-g), the smoothness of the layer has improved with increasing V/III ratio. At a relatively high V/III ratio of 1000, smooth morphology is achieved. Hence, the second layer grown with the combination of 600°C temperature and V/III ratio of 1000 was selected as the optimum layer for the nanowires growth. This double buffer layer structure has an average thickness of 72 nm excluding the irregular high terraces.
The above layer was annealed *in situ* at 700°C for 30 min under PH$_3$ flow to investigate possible crystal quality improvement. It can be seen from Figure 5.3 (h) that the layer has recrystallised making the surface rougher. These observations are quantitatively verified by AFM measurements. The initial nucleation layer has a RMS roughness of \(~6.6\) nm. This has improved to < 3 nm after the above discussed optimum second layer growth, but is again roughened after annealing to an RMS value of \(~8.2\) nm (Note that irregular high areas were not included in the roughness calculations for the double layers). Indeed, the terraces of the annealed layer also remain flat when compared to the size of the Au particles that are used for subsequent nanowire growth, although the height of the terraces vary in the longer range up to 200 nm.

The crystal structure of the initial, non-annealed and annealed layers is investigated using X-TEM and XRD. Figures 5.4 (a-c) show the low magnification X-TEM images of the initial layer, non-annealed layer and annealed layer, respectively. The diffraction pattern (Figure 5.4 (h)) and high resolution images (Figures 5.4 (d) and (e)) confirm the epitaxial
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Figure 5.4: (a) Low magnification X-TEM image of the initial buffer layer with red arrows indicating SFs parallel to the substrate and blue arrows indicating edge-on SFs inclined to the substrate. (b) Low magnification X-TEM image of the non-annealed double layers with the blue arrow indicating a SF that has propagated up to the surface. (c) Low magnification image of the annealed double layers with the dashed line indicating the boundary between heavily defective and defect reduced regions. (d) HRTEM image of the interface between Si substrate and initial InP layer with arrows indicating sporadic misfit dislocations. (e) HRTEM image of the interface between Si substrate and non-annealed InP double layers with arrows indicating periodic dislocations. (f) Strain map of (d). (g) Strain map of (e). (h) Selected area diffraction pattern from (b), showing the spots from regions twinned parallel to the substrate. (i) Schematic showing {111} planes that SFs can take place. All TEM images are taken along the <110> zone axis.

relationship of layers with the underlying Si substrate. As seen on the schematic in Figure 5.4 (i), there are four {111} planes on Si (111). When viewed along [1-10] zone axis, (1-1-1) planes parallel to the substrate surface (shown in red in the schematic) and one of the 3 other inclined type {111} planes ((-1-11) planes - shown in grey) can be viewed edge-on. When comparing the micrographs in Figures 5.4 (a) and (b), it can be seen that the initial layer consists of a very high density of stacking faults, along the {111} planes both parallel and inclined to the substrate surface. The parallel stacking faults are greatly reduced in the upper part of the double layer structure, which is the second layer. Some stacking faults which are inclined to the substrate surface have propagated with the second layer growth as
can be expected for a layer-by-layer growth parallel to the substrate. These stacking faults are not expected to affect nanowire growth significantly as the fraction of surface area terminated by the inclined stacking faults is very small compared to stacking fault-free area. Twinning can occur in all four of the above discussed \{111\} planes, especially during faceted island growth of the initial layer. The fringe pattern observed in the enlarged area in Figure 5.4 (b) are Moiré fringes arising from such 3-dimensionally twinned regions superimposed within the thickness of the TEM lamella.

In contrast to the study by Kang et al. [27], the annealed layer does not show further reduction in the number of SFs or thickness of the highly defective region, compared to the non-annealed layer. As seen in Figures 5.4 (d) and (f), the initial layer grows thicker than the critical thickness for the InP-Si lattice mismatched system [41] by forming misfit dislocations at the interface. Strain maps using the geometric phase analysis (GPA) technique [42] show that these dislocations are rather aperiodic, appearing from 2.2 to 7.5 nm. After the second layer is grown, the dislocations at the hetero-interface have become periodic (Figures 5.4 (e) and (g)) with a separation of 4.84 ± 0.7 nm. After the additional annealing step, the period of misfit dislocations is reduced to an average of 4.51 ± 0.6 nm, which is quite close to the theoretically calculated value of 4.46 nm, for a fully relaxed InP layer on Si (111) substrate. It seems that during the initial layer growth at low temperature, the strain is partially and unevenly relaxed forming sporadic dislocations. During the heat up and the second layer growth at high temperature of 600°C, the dislocations at the heterointerface move and the layers relax almost fully and evenly; leaving only a small amount of residual strain. The improvement after annealing is not significant enough to exhibit discernible improvement in the crystal quality. The measured lattice spacing between the (111) planes in the non-annealed double buffer layer structure is 3.4 Å, which is very close to the expected value for bulk InP of 3.38 Å. This again confirms that the layer is relaxed before the annealing step.

The XRD rocking curve taken for the [111] reflections of the non-annealed layer fits well with a simulated 60 nm thick, 100% relaxed InP layer as shown in Figure 5.5 (a). The discrepancy in thickness between XRD and SEM measurements could be due to the local height variations arising from the terraced regions. Reciprocal space map (RSM) for the [115] asymmetric reflections of the same layer (Figure 5.5 (b)) shows that the Si substrate and the buffer layer peaks lie along the same ω value. This again confirms that the layers are fully relaxed before the additional annealing step and the reciprocal space map also shows no strain gradient across the thickness of the layer in agreement with the TEM observations.
High Vertical Yield InP Nanowire Growth on Si (111) Using a Thin Buffer Layer for Integration with Si Technology

As shown in Chapter 2.3, for III-V materials the (111) is a polar surface and when grown on a non-polar group IV substrate like Si, the layers could grow as (111)A, (111)B or a mix of these two types giving rise to inversion domains. Br₂:methanol solution etches InP (111)B much faster than (111)A [43]. Hence the etch rate of the buffer layer in this solution compared to that of InP (111)B and A substrates can be used to identify the polarity of the layer. Due to the same etch rate difference, the etch pits will also show an undercut for InP (111)A and an overcut for InP (111)B [31]. The etch rate experiments in 0.1% Br₂:methanol solution show that these buffer layers are of (111)B polarity. Cross section SEM of the etch pits in the buffer layer sample that was dipped in 0.1% Br₂:methanol solution also revealed an overcut shape as shown in Figure 5.6 (a). Before the buffer layer growth, the oxide free substrates were annealed at 750°C and then cooled down to initial layer growth temperature of 375°C. Studies carried out in ultra-high vacuum conditions have shown that during this cool down process, a Si(111)1×1 reconstructed surface is expected to form below 400°C [44]. When exposed to PH₃, the outer most layer of atoms of the top bilayer in Si(111)1×1 is replaced by P atoms [45] creating a pseudo (111)B surface as shown in Figure 5.6 (b). Similar group V replacement of Si atoms takes place even when both precursors (group III
Nanowires are turned on together as in the current case, due to the chemical stability of the group V termination [46]. Thereafter, as shown in Figure 5.6 (b), the (In-P) bilayers form on the P-terminated Si surface resulting in a (111)B InP layer as observed here. The B polarity throughout the layer is again confirmed by comparison with nanowires grown on InP (111)A and (111)B substrates in the next section.

5.4 Nanowires

Nanowires were grown on the buffer layers, InP (111)A and B substrates, and Si (111) substrates in the same growth run, at the temperature of 420°C and V/III ratio of 350. According to previous studies, these growth conditions result in predominantly WZ phase nanowires [32]. Figure 5.7 shows SEM images of the nanowires grown on the bare Si substrate, InP (111)B substrate, InP (111)A substrate and the non-annealed buffer layer, respectively. As seen in Figure 5.7 (a), on bare Si substrate, whisker and island growth is prominent, giving very low overall nanowire yield. The nanowires are kinked and more importantly, the growth direction is random with extremely poor vertical yield. Vertical yield on the InP (111)B substrate is 100% and over 97% on the buffer layer. Figure 5.7 (e) shows a top view of Figure 5.7 (d), with vertical nanowires seen as bright white dots and non-vertical wires (marked by arrows) clearly visible against the buffer layer. The inset shows a X-SEM view of the nanowires with the Si substrate and buffer layer visible. The density of nanowires on the buffer layer is slightly higher than that on InP (111)B substrate. The average density of nanowires on the buffer layer is 0.67 μm⁻², whereas the density on the InP substrate is 0.54 μm⁻². This is due to the slightly higher adherence of Au particles to the rougher buffer layer surface (RMS roughness ~3 nm) compared to the commercially polished InP substrate (RMS roughness < 0.5 nm).

The two sets of nanowires also show a difference in length. The length of the nanowires grown on the InP (111)B substrate is 6.4 ± 0.4 μm, whereas the length of those grown on the InP buffer layer is 7.6 ± 0.3 μm (for the same 30 nm Au particle diameter).
Both, the slightly higher nanowire density and the increased surface roughness should lead to shorter nanowires in the case of growth on the buffer layer, which is contrary to what is observed. The possible mechanisms that could play a role in this increased growth rate on the buffer layer include the synergetic effect, that has been previously observed for III-V nanowires [47], or differences in the oxide layer properties between the epi-ready InP substrate and the native-oxide covered buffer layer [48, 49]. In order to test the hypothesis of the surface oxide, nanowires were grown on InP (111)B substrates and the buffer layer after removing any surface oxides by etching in 10% H₃PO₄ acid for 2 min. The growth rate of nanowires on both substrates increased compared to the reference samples from which the oxide was not removed. However, the increase in the growth rate on InP substrate indeed was higher than that on the buffer layer reducing the percentage difference from ~19% (above) to ~8%. The reduction in difference in length suggest that the differences in surface oxides could be playing a role in increased growth rate of nanowires on the buffer layer up to
some extent. On the other hand, the remaining 8% difference suggests that oxide cannot be the only cause. It is most probably a combinational effect of few different factors that leads to this observation, although not completely clear at this stage.

The variation of nanowire length across the buffer layer sample is negligible and is more or less similar to the variation seen on the InP (111)B substrate. This shows that there is no significant impact on the nanowire morphology from the presence of step edges and height differences in the terrace structures of the buffer layer.

Nanowire growth on InP (111)B and A substrates are significantly different as seen in Figures 5.7 (b) and (c). As confirmed by top and side view images, the nanowires on InP (111)A are predominantly growing along the <111>B directions which are at an angle of 19.5° with respect to the substrate surface and exhibit a trigonal symmetry from the top view. In addition, there are nanowires growing in <110> and <112> directions as well as kinked wires growing in irregular directions. There is also a smooth 2D layer growth in between the nanowires on the substrate as can be clearly seen in the inset of Figure 5.7 (c). The nature of nanowire growth on the buffer layer compared with that on the InP (111)A and B substrates further confirms that the buffer layer is behaving entirely as an InP (111)B substrate and shows no presence of (111)A domains. As these buffer layers grown on Si(111) are entirely of B polarity, they are free of inversion domains.

The optical properties of InP nanowires grown on InP (111)B substrates have been extensively investigated [50, 51]. It is important that these properties are maintained when the nanowires are grown on the buffer layer in order to fabricate high quality optoelectronic devices on the Si. PL spectra were obtained from ensembles of nanowires grown on InP (111)B substrates and the buffer layer on Si at room temperature. As seen in Figure 5.7 (f), the spectra are similar and show emission at 1.46 eV. This energy corresponds exactly to the transition from the conduction band to the split-off valence band of WZ InP, which is ~ 30 meV lower than the first valence band [51] as discussed in Chapter 2.7. Also note that the slight differences in the line widths of the two plots are due to differences in physical nanowire distribution, arising from the dry mechanical transfer process to bare Si substrates before measurement.

Apart from minor differences in density and length, the nanowires grown on the buffer layer are identical to the nanowires grown on InP substrate in terms of morphology and optical properties. TEM studies have also been performed on the two types of nanowires and they are both of WZ crystal phase with similar densities of stacking faults. Other growths (not shown here) have been carried out on the buffer layer at different growth conditions and it is found that the properties of the nanowires are same as of those grown homoepitaxially for the particular growth condition. Nanowires were also grown on the annealed buffer layer (not shown here), and they are similar to those grown on the non-annealed buffer layer in terms of percentage of vertical yield, morphology, crystal structure and optical properties.
5.5 Summary

In summary, growth of InP nanowire on Si (111) substrates is demonstrated using a thin InP buffer layer. A two-step growth process is used for the growth of the buffer layer. A low temperature and a very high V/III ratio are needed for the nucleation of the initial layer on Si. The choice of temperature and V/III ratio is again important during the second layer growth in order to achieve smooth morphology with minimal layer thickness. It is found that the additional post growth annealing step does not improve the crystal quality of the layer noticeably, as most of the relaxation had already taken place during the second layer growth. The buffer layer is (111)B oriented and shows stacking faults both parallel and inclined to the substrate. The vertical yield of nanowires on the buffer layer is over 97%. The morphology and optical properties of the nanowires grown on this buffer layer on Si substrates are very similar to those grown on InP (111)B substrates. It is also seen that the crystal defects of the buffer layer do not have a significant effect on vertical yield or the properties of the nanowires. This means that the intermediate buffer layer approach provides an option to grow InP nanowires on Si, with the possibility of directly adopting growth parameters from the homoepitaxial growth system for the desired result. Additionally, in the current case of Au seeded nanowires, the buffer layer prevents the contact of Au with the Si substrate. Hence, this opens up the opportunity to replicate phase perfected InP nanowires [50] and their applications [3, 4, 6] on Si, for future microelectronic compatible devices, in a much easier and better way than by direct growth on bare Si substrate.

5.6 References


High Vertical Yield InP Nanowire Growth on Si (111) Using a Thin Buffer Layer for Integration with Si Technology


Chapter 6

Nanowires Grown on (100) InP Substrates: Growth Directions, Facets and Crystal Structures

Overview: Nanowires are generally grown on (111) substrates mainly due to the ease of achieving uniform vertical growth. However, nanowires are almost the only type of structures that are exclusively grown on (111) substrates. Almost all other main types of structures like planar structures, quantum dots and structures grown on patterned substrates such as v-grooves are grown on (100) substrates, which also is the industry standard orientation. Therefore, it is essential that nanowires can be grown on (100) substrates if the nanowire devices are to be seamlessly integrated with other devices forming complete, functional, mass scale producible integrated circuits on a single chip. Yet, seemingly complex ensembles of nanowires grown on (100) substrates are not well understood. This chapter presents a comprehensive study on the nanowires grown on InP (100) substrates in terms of growth directions, facets and crystal structures, forming a solid knowledge base that provides a deeper understanding of the structural aspects of nanowires grown on this unconventional crystal plane.

6.1 Introduction

Since the first observation of catalysed whisker growth by Wagner and Ellis [1], semiconductor nanowires have been grown and studied on surfaces with different crystal orientations. Among these, for cubic semiconductor materials, the (111) surface is far more commonly used, due to the lower surface free energy of this surface that promotes easy formation of vertical nanowires [2-5]. As shown in Chapter 2.1 one problem with vertical nanowires grown on (111) substrates is the formation of stacking faults due to the stacking sequence of face centred cubic materials in the <111> direction. This problem is very much prominent in InP, which has the lowest stacking fault energy out of the common cubic III-V semiconductors [6, 7], making the realization of pure crystal phase nanowires difficult, and in particular achieving defect-free ZB <111> nanowires almost impossible. Vertical
nanowires grown on (100) substrates, that is nanowires adopting the [100] crystal orientation, are known to have the major advantage of being twin or stacking fault-free [8-11], despite the difficulty in achieving growth in this energetically unfavourable direction. Hence, it provides an opportunity to grow planar defect-free ZB InP nanowires. Most importantly, (100) is the standard substrate orientation used in industry, and the ability to grow vertical nanowires on (100) substrates is essential for the seamless integration of InP nanowire devices with other planar electronic and photonic devices on a single chip.

A number of groups have grown III-V nanowires on (100) substrates [9-22]. It is seen that there is a considerable yield of non-vertical nanowires growing in various directions, unless the nanowire nucleation is tightly controlled [10]. The knowledge of these other growth directions and the properties of such nanowires are important in maximizing one growth direction over the other, and particularly in maximizing the vertical yield. The understanding of nanowire facets, especially the side-facets, provides novel facet profiles and cross sectional shapes for engineering radial heterostructures. Information on the crystal structure and phase is also essential, as it affects not only the optical quality but also the band-gap. Nevertheless, extensive studies have not been carried out investigating these properties.

In the current chapter, an in-depth analysis into the seemingly complex growth directions of InP nanowires that are grown on InP (100) substrates is presented. Three main types of nanowires, namely vertical, non-vertical and planar, are identified to be growing on the (100) substrates. In addition to growth directions, the side facets, growth facet and the crystal structure of each of these types are investigated in detail. A mathematical model based on the 3-dimensional twinning concept [23] is presented to explain the non-vertical nanowire growth directions and the model is verified by the experimental results. It is shown that 99% of the nanowires grown on InP (100) substrates grow along either <100>, <111> or <110> direction driven by either a {100} or {111} growth facet, which is not perpendicular to the growth direction in the case of planar nanowires. It is also found that NWs with differing crystal structures can grow simultaneously, bringing further potential for bandstructure engineering on the same substrate compared to planar structures.

### 6.2 Experimental Methods

All samples were prepared immediately prior to growth by dispersing 30 nm colloidal Au particles on poly-L-lysine (PLL) coated (100) InP substrates. A (111)B InP substrate prepared using the same method was also included in each growth run as a reference. All samples discussed in this chapter were annealed for 10 min under PH$_3$ flow at or below the relatively low temperature of 450°C (unless specified otherwise) in order to enhance alloying
between the substrate and the Au particle before initiating nanowire growth. The TMIn flow used for the growths was $2.015 \times 10^{-6}$ mol/min, yielding a 1 μm/hr growth rate for vertical nanowires. A number of samples grown at different temperatures and V/III ratios were analysed for the work presented in this chapter. The exact growth parameters of the relevant samples are given under each section. A more comprehensive study on the effects of the pre-growth annealing and growth conditions on the nanowires is presented in Chapter 7.

Nanowires were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Cross-sectional TEM (X-TEM) samples of the planar nanowires were prepared by tri-pod polishing technique. Lateral cross sections of the vertical nanowires were prepared by microtome sectioning.

### 6.3 Main Types of Nanowires Grown on InP (100) Substrate

Figure 6.1 (a) shows a SEM image of a typical nanowire sample catalysed by colloidal Au particles. Three main types of nanowires can be identified: (1) vertical nanowires (indicated by blue arrows), (2) non-vertical nanowires that grow at an inclined angle with respect to the substrate surface (yellow arrows) and (3) planar nanowires that grow along the substrate (red arrows). It is worth investigating these three types of nanowires that grow on (100) substrates in detail. In the following section, growth directions, facets and crystal structure of each of these types of nanowires will be discussed. For in-depth analysis of the types of nanowires, a sample consisting of 83% vertical nanowires, 7% non-vertical nanowires and 10% planar nanowires was selected as the principal sample. The sample was grown at 450°C temperature under a V/III ratio of 350. However, other samples with different relative yields (as specified when required) were also considered in order to obtain an overall understanding.

#### 6.3.1 Vertical Nanowires

Figures 6.1 (b) and (c) show 45° tilted and top views of vertical nanowires of the principal sample, respectively. The side facets of the vertical nanowires can be \{100\}, \{110\} or a combination of the two (resulting in an octagonal cross-section) depending on the growth condition and the particle size. Here, they broadly appear to be of \{100\} type for the nanowires grown at 450°C as seen in Figure 6.1 (c). Figure 6.1 (d) shows a typical vertical nanowire from a sample grown at 425°C and V/III of 350, showing an octagonal cross-sectional shape with \{110\} and \{100\} side facets. X-TEM analysis was carried out in order to ascertain the side facet evolution along the vertical nanowires shown in Figures 6.1 (b) and (c). The TEM images of the cross sections taken across the top most area with the Au particle, area just below the particle and bottom of the nanowires are shown in Figures 6.1(f), (g) and (h), respectively. Cross section TEM image of the top most area indicates that the
growth facet just below the Au particle has an octagonal shape. The octagon comprises of four \{100\} facets and four \{110\} facets. In this case, the lateral growth of \{110\} facets is faster than that of \{100\} facets and a square cross section comprising of \{100\} facets is formed towards the bottom of the nanowire as a result of lateral overgrowth.

Yet, as seen in Figure 6.1 (g), the lateral overgrowth of the two types of \{110\} facets that are orthogonal to each other does not take place at the same rate. (011) and (0-1-1) facets grow faster than (01-1) and (0-11) side facets. \{011\} planes are non-polar, meaning...
§ 6.3 Main Types of Nanowires Grown on InP (100) Substrate

they have an equal numbers of group III and V atoms terminating the surface. However, in order to explain the above anisotropy, one has to consider the two orthogonal (011) and (01-1) planes with a slight angle towards the top of the nanowire as it would be in a tapered nanowire. As shown in Figure 6.2, although the {011} planes are non-polar on their own, the step structure formed by an incline would show a partial polarity with uneven numbers of group III and V atoms on the surface. This partial polarity is group III rich (A - polar) for (011) and (0-1-1) facets, and group V rich (B - polar) for (01-1) and (0-11) facets. Under group V rich, high V/III ratio growth conditions similar to those used in this study, the growth of “A” type facets takes place much faster than “B” type facets [24-26]. Hence, during the lateral growth and tapering of the nanowire, the (011) and (0-1-1) side facets grow faster than (01-1) and (0-11) side facets resulting in an elongated octagonal shape cross section towards the top-mid area of the nanowire as seen in Figure 6.1 (g).

Figure 6.2: Formation of partially polar surfaces on the {011} nanowire facets with tapering. (a) Non-polar (011) facet. (b) (011) facet with a slight angle towards the nanowire growth direction, showing a partially A polar surface. (c) (01-1) facet with a slight angle towards the nanowire growth direction, showing a partially B polar surface.
A closer look at the Figure 6.1 (d) reveals that a similar anisotropy of growth rates in the two \{110\} directions may even prevail along the entire length of the nanowire, when \{110\} facets are predominant. This suggests that a rectangular cross section shape is possible in addition to the reported square shape \([11]\) for the four \{110\} type side facets. This is most likely to be observed at high V/III growth conditions as discussed above. Dependence of the nanowires side facets on the growth conditions and control of facets are discussed more in detail in Chapter 7. Table 6.1 summarises the possible, simple, low index facet combinations and cross-sectional shapes for vertical nanowires on (100) substrates. It should be noted that the four \{100\} facets are always uniform since there is no effect of polarity on these facets.

<table>
<thead>
<tr>
<th>Facet combination</th>
<th>Cross sectional geometry</th>
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<tbody>
<tr>
<td>1</td>
<td>Four {100} facets</td>
</tr>
<tr>
<td>2</td>
<td>Four {110} facets</td>
</tr>
<tr>
<td>3</td>
<td>Combination of {100} and {110} facets</td>
</tr>
</tbody>
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\(^7\) Here, \((011)\) and \((0-1-1)\) facets have been completely overgrown, while \((0-11)\) and \((01-1)\) facets still remain. This could mostly form as an intermediate stage during lateral growth of facets.

Table 6.1: Possible low index facet combinations and cross sectional shapes for vertical nanowires on (100) substrates.
The growth facet of these vertical nanowires is the (100) facet that is parallel to the substrate (as indicated by the black arrow in Figure 6.1 (e)) and it should be noted that it is not a combination of \{111\} lower energy facets as seen in some $<100>$ nanowires [4]. The crystal structure of these vertical nanowires is defect-free ZB, in agreement with the previous reports [9-11, 27]. Note that defect-free ZB phase formation of $[100]$ nanowires that has the growth facet parallel to the substrate was explained in Chapter 2.2.

The non-vertical nanowires are discussed next and their growth directions are derived using a 3-dimensional multiple order twinning model.

6.3.2 Non-Vertical Nanowires

As seen in Figure 6.3 (a), the non-vertical nanowires that grow inclined to the surface, may initially seem randomly oriented. However, close inspection reveals that a vast majority of these non-vertical nanowires can be broadly divided into two major sub-types, differentiated by their morphology and dimensions: Type 1, less tapered longer nanowires (Figure 6.3 (b)) and Type 2, more tapered shorter nanowires (Figure 6.3 (c)) whose morphology is similar to vertical $[100]$ nanowires.

These in fact are $<111>$ and $<100>$ nanowires respectively, which acquire a non-vertical growth directions due to the 3-dimensional twinning that takes place at the bottom of the nanowire. The two types are illustrated in Figure 6.3 (d), with extended vertical segments for clarity. The two types are characterised in detail in the following sub-sections.

6.3.2.1 Type 1

Most of the nanowires with Type 1 morphology grow along the 2 directions that are parallel to the (011) cleavage plane and make $35^\circ$ angle with the substrate surface. From crystallography, it can be easily concluded that these are nanowires that grow in 2 of the 4 $<111>$ directions that project out of the (100) substrate. Yet, there is a minority of nanowires that do not fit the direct $<111>$ growth directions when considering the angles they create with the surface and the cleavage plane.

Uccelli et al. have shown that the unusual non-vertical growth directions seen in self-catalyzed GaAs nanowires grown on Si (111) can be explained by 3-dimensional multiple-order twinning of the seed particle [23]. Here this model is extended for nanowires growing along the $<111>$ directions after twinning in \{111\} planes on the (100) substrate by transforming the axis system to suit the (100) substrate. An atomistic model is shown in Figure 6.4 for the easy visualisation of the concept. The untwinned \{111\} half octahedron and one possible 3-dimensionally twinned octahedron is shown with respect to the (100) substrate. Black and yellow arrows indicate the possible direct $<111>$ growth directions (1st order) and $<111>$ growth directions after one 3-dimensional twin (2nd order), respectively.
The calculation of the growth directions with respect to the substrate is shown in the following section.

**Figure 6.3:** (a) A top view SEM image of a typical nanowire sample grown on InP (100) substrates, showing the seemingly random growth directions of the non-vertical nanowires. (b) SEM image of a non-vertical nanowire with a less tapered and long morphology, with the inset showing the top view of two similar nanowires. (c) A non-vertical nanowire with a more tapered morphology, similar to vertical nanowires, with the inset showing the top view of similar nanowires. (d) The two types of non-vertical nanowires, illustrated with extended untwinned [100] vertical segments for clarity.

**Figure 6.4:** An atomistic model showing the possible 1st and 2nd order twinned <111> growth directions: black solid arrows showing 1st order growth directions from the untwinned primary crystal and yellow solid arrows showing the 2nd order <111> directions from the twinned crystal.
6.3.2 Growth direction calculation for 3-dimensional multiple order twinned nanowires

The Householder transformation can be used to obtain the reflection about a plane containing the origin [28]. Since a twin plane also acts as a mirror creating the mirror image of the crystal before and after the twin plane, the Householder matrices for the \( \{111\} \) planes, inverted with respect to the origin can be used to model twinning in 3-dimensional space [23]. As the twinning takes place also around \( \{111\} \) planes in the current case, the same Householder reflection matrices derived in ref [23] (given below) can be used to derive the growth directions of the nanowires after multiple order twinning.

\[
T_{(111)} = \begin{pmatrix} -1 & 2 & 2 \\ 2 & -1 & 2 \\ 2 & 2 & -1 \end{pmatrix} \quad T_{(1\bar{1}1)} = \begin{pmatrix} -1 & -2 & -2 \\ -2 & -1 & 2 \\ -2 & 2 & -1 \end{pmatrix}
\]

\[
T_{(\bar{1}11)} = \begin{pmatrix} -1 & -2 & 2 \\ -2 & -1 & -2 \\ 2 & -2 & -1 \end{pmatrix} \quad T_{(\bar{1}\bar{1}1)} = \begin{pmatrix} -1 & 2 & -2 \\ 2 & -1 & -2 \\ -2 & -2 & -1 \end{pmatrix}
\]

The growth direction \( t_{i,j} \) is calculated by multiplying the relevant sequence of transformations \( T_j \) by the possible growth directions \( d_i \) with respect to the final twinned crystal, similar to ref [23]. For example, the first 3 orders can be written as:

1\textsuperscript{st} order: \( t_i = d_i \) no twinning has taken place \hfill (6.1)

2\textsuperscript{nd} order: \( t_{i,j} = (T_j)d_i \) twinned once, 3-dimensionally across \( j^{th} \) \( \{111\} \) plane \hfill (6.2)

3\textsuperscript{rd} order: \( t_{i,j,k} = (T_jT_k)d_i \) twinned twice, 3-dimensionally, where \( T_j \) and \( T_k \) are transformation matrices corresponding the \( j^{th} \) and \( k^{th} \) \( \{111\} \) twinning planes. \hfill (6.3)

In order to ascertain the growth direction of the nanowires growing in the <111> directions after twinning, \( d_i \) is substituted with the possible <111> directions.

6.3.2.3 Calculation of elevation (\( \alpha \)) and azimuth (\( \varphi \)) angle with respect to the (100) substrate

An axis system needs to be defined in order to verify the calculated growth directions of the nanowires experimentally, using angles they make with the (100) substrate. These are defined with respect to the \( \{110\} \) natural cleavage planes due to ease of identification of these two planes as references. The axis system and the definition of angles (\( \alpha \) – elevation angle created with the substrate surface and \( \varphi \) - the azimuth angle with respect to the \( \{110\} \) cleavage planes) are illustrated in Figure 6.5. For seamless continuation and clarity, the same symbols used in ref [23] are used in this derivation, where appropriate.
Figure 6.5: Projections of the nanowire on the x, y, z axis system on (100) substrate.

As shown in Figure 6.5, once the nanowire growth direction $t$ is determined, the elevation angle $\alpha$ and the azimuth angle $\varphi$ can be calculated using $t$’s projections on the axis system defined for the (100) substrate. The projections are:

Projection on $x$ ([011] direction) axis: \[ P_x = \frac{x}{\sqrt{|t|}} \] (6.4)

Projection on $y$ ([01-1] direction) axis: \[ P_y = \frac{y}{\sqrt{|t|}} \] (6.5)

Projection on $z$ ([100] direction) axis: \[ P_z = \frac{z}{\sqrt{|t|}} \] (6.6)

Therefore; \[ \alpha = \tan^{-1} \left( \frac{P_x}{\sqrt{P_x^2 + P_y^2}} \right) \] (6.7)

and \[ \varphi = \tan^{-1} \left( \frac{P_y}{P_x} \right) \] (6.8)

Table 6.2 summarizes all the possible growth directions of 3-dimensional twinned $<111>$ nanowires up to the 3rd order, calculated using the above model. Twinning in both A and B polar $\{111\}$ planes and nanowires growing with both A and B polarities are considered possible in the calculations for completeness. The “order” is determined by the number of times the growth direction has been transformed and refers to the number of times it has twinned. For example, 1st order directions are not twinned at all and 2nd order directions are obtained after twinning once. The number of possible growth directions increases exponentially with the order of twinning. However it should be noted that consecutive twinning across the same $\{111\}$ plane does not give rise to a new growth
### § 6.3 Main Types of Nanowires Grown on InP (100) Substrate

<table>
<thead>
<tr>
<th>Order</th>
<th>$\alpha$</th>
<th>$\varphi_{[111]}$</th>
<th>$\varphi_{[101]}$</th>
<th>Polarity of NW</th>
<th>Notes</th>
<th>Experimental frequency of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.26</td>
<td>-90, 90</td>
<td>0, 180</td>
<td>B</td>
<td>NWs grown in $&lt;111&gt;$ directions on (100) without 3D twinning</td>
<td>89%</td>
</tr>
<tr>
<td>2</td>
<td>74.21</td>
<td>-90, 90</td>
<td>0, 180</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.10</td>
<td>-56.31, -123.69, 56.31, 123.69</td>
<td>33.69, -33.69, 146.31, -146.31</td>
<td>A</td>
<td>Twinned once 3 dimensionally in a ${111}$ plane and then grown in $&lt;111&gt;$ directions</td>
<td>7%</td>
</tr>
<tr>
<td>3</td>
<td>35.26</td>
<td>-90, 90</td>
<td>0, 180</td>
<td>B</td>
<td>Repetition of 1st order angles due to even number of consecutive twins</td>
<td>Counted as 1st order due to indiscernibility</td>
</tr>
<tr>
<td>3</td>
<td>44.88</td>
<td>-129.81, 129.81, -50.19, 50.19</td>
<td>-39.81, 39.81, 140.19</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>56.51</td>
<td>9.46, 9.46, 170.54, 170.54</td>
<td>99.46, 99.46, 99.46</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>56.51</td>
<td>-99.46, -170.54, 80.54, 80.54</td>
<td>-9.46, 9.46, 9.46</td>
<td>A</td>
<td></td>
<td>4%</td>
</tr>
<tr>
<td>3</td>
<td>26.68</td>
<td>23.96, 23.96, -113.96, -156.04</td>
<td>113.96, 113.96, 66.04</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>26.68</td>
<td>-113.96, -66.04, 113.96, 66.04</td>
<td>-23.96, 23.96, 23.96</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18.71</td>
<td>-16.7, -163.3, 106.7, 16.7</td>
<td>73.3, -73.3, 163.3</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18.71</td>
<td>-73.3, 73.3, -106.7, 106.7</td>
<td>16.7, -16.7, -163.3</td>
<td>A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.2:** Growth directions of 3-dimensional twinned $<111>$ nanowires grown on InP (100) substrates up to the 3rd order.
direction for the <111> direction that is perpendicular to that particular plane, which effectively becomes 1-dimensional twinning. These are not considered as higher order scenarios in Table 6.2.

For the other three <111> directions, an odd number of consecutive twins across the same plane would give rise to a new direction as the growth is non-perpendicular to the twinning plane. Yet, this direction would be same as the lower order direction derived after a single twin across the {111} plane that consecutive twinning took place. An even number of twinning across the same plane would create “the mirror image of a mirror image effect”, rotating them 360° and resulting in the same orientation as the untwinned nanowire. In mathematical terms, the \( n^{th} \) higher order twinned growth directions include the \((n-2m)^{th}\) lower order directions (where \( n \) and \( m \) are integers), due to the repetition of angles with an even number of consecutive twinning on the same {111} plane. This becomes clear when comparing 1st and 3rd order growth directions in Table 6.2.

These expected growth directions are experimentally corroborated by the angles measured of the non-vertical nanowires in the principal sample. The projection angle measurements were taken on individual nanowires with respect to the cleavage planes and substrate normal by rotating and tilting in the SEM. The experimental frequency of occurrence as a percentage out of the total Type 1 non-vertical nanowires are given in the last column of Table 6.2. The frequency of occurrence decreases with the order of twinning.

However, it should be noted that due to the repetition of angles after an even number of twinning across the same plane, a particular nanowire that shows a lower order twinned direction could be containing consecutive twins across the same plane and therefore could actually be of a higher order. For the current analysis, it is deemed fair that the nanowires belong to the lowest possible order for the particular combination of angles, due to the decreasing probability of occurrence of consecutive twins across the same plane with the increasing number of other possibilities at higher orders. Indeed, a few of these nanowires counted as lower orders could actually be of higher orders. It should also be noted that all <111> nanowires measured in the current study are of B polarity, meaning they only grow along the <111>B directions.

Nanowires grown in the <111> directions generally have a significantly higher growth rate compared to those grown in the <100> direction, similar to the reference nanowires grown on InP (111)B substrates in the same growth run. Figure 6.6 (a) shows a 1st order <111> nanowire imaged 35° tilted to the {110} cleavage plane, so that the electron beam is parallel to the nanowire axis. As shown in this figure, the side facets form a hexagonal shape with a hexagonal or truncated triangular tapered bottom that is typically seen for nanowires grown on (111) substrates. By considering the inter-planar angles the nanowire facets make
with the substrate and the $\{110\}$ cleavage plane, they are derived to be $\{112\}$ facets. This is also similar to the reference nanowires grown on InP (111)B substrate under the same growth conditions which show $\{112\}$ type side facets (inset of Figure 6.6 (a) shown with respect to the $\{110\}$ cleaved edge).

Once growth in the $<111>$ direction is initiated, it is comparable to the growth on (111) substrates. Twin planar defects perpendicular to the growth direction can now be easily created and hexagonal wurtzite (WZ) phase can also form depending on the growth conditions. As shown in Chapter 2.1, this is owing to the fact that in $<111>$ directional growth, each new layer can nucleate in a ZB or WZ position, independent of the previous stacking sequence (given the formation energy requirement is satisfied) [29]. Figure 6.6 (c) shows a TEM image of a $<111>$ nanowire grown on InP (100) substrate. As the growth orientation information is lost during the sample preparation process for TEM analysis, they are initially identified as $<111>$ oriented nanowires by matching the morphology as seen in Figure 6.6 (b). This is later verified by indexing the diffraction patterns. The non-vertical nanowires grown along $<111>$ directions are of WZ crystal phase with some stacking faults; again, similar to those grown vertically on InP (111)B substrates under the same growth conditions. Hence, the actual facets of the nanowires are of $\{1\text{-100}\}$ type which is the equivalent of ZB $\{112\}$ planes in the WZ phase.

Figure 6.6: (a) A 1$^{st}$ order $<111>$ non-vertical nanowire viewed along its growth axis, showing the $\{1\text{-100}\}$ ($\{112\}$ ZB equivalent) side facets, inset shows a nanowire with respect to the $\{110\}$ cleavage plane from the reference sample grown on InP (111)B substrate under the same growth conditions (b) Low magnification image of the nanowire shown in (c), nanowires are initially identified as $<111>$ by matching the morphology. (c) High resolution TEM image showing the defective WZ crystal structure of a $<111>$ non-vertical nanowire and the inset shows the diffraction pattern in the $<1\text{-20}>$ zone axis.
<111> nanowires are the most commonly reported type of non-vertical nanowires that grow on (100) substrates [11, 15-20]. However, in the current case, it is found that depending on the growth conditions, up to about 60% of the non-vertical nanowire growth directions could not be explained by direct or multiple order twinned <111> growth directions; that is by the “Type 1” scenario. By inspecting the morphology, one could also see that these unexplained nanowires are generally of above mentioned Type 2.

6.3.2.4 Type 2

Here, the 3-dimensional multiple order twinning takes place on {111} planes, similarly to the previous case. However after twinning, the nanowires grow in <100> directions instead. This scenario can be visualised as shown in the atomistic model in Figure 6.7 (a), where 3 possible <100> directions (indicated by yellow arrows) are available for growth from the resulting twinned crystal. Figures 6.7 (b) and (c) show a 3-D computer model and an SEM image of a 2nd order Type 2 nanowire viewed at the same tilt angle with respect to the substrate, respectively. The {111} planes are showed in the model for clarity and comparison. The existence of the twin plane can be identified in the SEM image due to the difference in lateral over-growth at the twin plane.

![Figure 6.7](image)

**Figure 6.7:** (a) An atomistic model showing the 1st and 2nd order non-vertical <100> growth directions; 1st order directions are shown by black solid arrows from the untwined primary crystal and 2nd order <100> directions by yellow solid arrows from the twinned crystal. (b) – (c) A 3D model and an SEM image of a 2nd order non-vertical Type 2 nanowire making $\alpha$ and $\varphi_{[011]}$ angles of 42° and 108°, viewed along the same direction and tilt for comparison. The half {111} octahedron of the initial and twinned crystals are shown for the ease of comparison with the atomistic model in (a) and understanding of the evolution of nanowire growth direction by twin formation.
The possible growth directions with respect to the substrate can be calculated using the same model used before, **simply by substituting \( d \) with all possible \(<100>\) directions.** Table 6.3 shows all possible growth directions for 3-dimensional multiple order twinned \(<100>\) nanowires up to the 3\(^{\text{rd}}\) order. Considering the angles in Table 6.3, it is clear that the vertical nanowires that were considered as a main type, are in fact a special case of 1\(^{\text{st}}\) order Type 2 non-vertical nanowires.

An odd number of consecutive twinning about the same \{111\} plane (1-dimensional twinning) gives rise to new growth directions for all three \(<100>\) growth orientations, as none of the growth directions are perpendicular to the twinning plane in this case. However, similar to the \(<111>\) case, this growth direction will be same as the lower order direction derived after a single twin across the \{111\} plane that consecutive twinning took place. Again, similar to the \(<111>\) case, an even number of such consecutive twinning around the same plane negates each other’s rotation, giving the same directions as the untwinned direction. These repeating angles are included in Table 6.3 (see 1\(^{\text{st}}\) and 3\(^{\text{rd}}\) order growth directions). It should also be noted that this means some of the vertical nanowires could have an even number of consecutive inclined twins at the base of the nanowire.

Experimentally measured angles of the individual Type 2 non-vertical nanowires confirm the presented model. The relative frequency of occurrence against the order of twinning is given as a percentage out of the total Type 2 non-vertical nanowires in Table 6.3. At first glance it may appear as if the majority of the Type 2 non-vertical nanowires are of the 2\(^{\text{nd}}\) order, which accounts for 62\%. However, one should not forget that the vertical nanowires are also a variant of 1\(^{\text{st}}\) order Type 2 nanowires, and they are not included in the statistics in Table 6.3. The considered principal sample contains a high yield of 83\% vertical nanowires and when considered with these, the general trend of decreasing frequency of occurrence with increasing order remains true for this particular sample.

<table>
<thead>
<tr>
<th>Order</th>
<th>( \alpha )</th>
<th>( \Phi_{[11]} )</th>
<th>( \Phi_{[1-1]} )</th>
<th>Notes</th>
<th>Experimental frequency of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>–</td>
<td>–</td>
<td>Vertical nanowires – considered a main type</td>
<td>Not included in the statistics</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>-45 135 45</td>
<td>-45 -135 45</td>
<td>Other (&lt;100&gt;) non-vertical nanowires without any 3D twins</td>
<td>20%</td>
</tr>
<tr>
<td>2</td>
<td>41.81</td>
<td>-161.57 108.43</td>
<td>-161.57 108.43</td>
<td>Twinned once 3 dimensionally on a {111} plane and then grown in (&lt;100&gt;) direction</td>
<td>62%</td>
</tr>
</tbody>
</table>
The morphology and growth rate of non-vertical <100> nanowires are similar to those of the vertical [100] nanowires. The inset of Figure 6.8 (a) shows the same 2\textsuperscript{nd} order, Type 2 non-vertical nanowire shown in Figure 6.8 (a), but imaged 72° rotated from the (011) cleavage edge and 48° tilted to the vertical so that the electron beam is parallel to the

### Table 6.3: Growth directions of 3-dimensional twinned <100> nanowires grown on InP (100) substrates up to the 3\textsuperscript{rd} order.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>90</th>
<th>180</th>
<th>-90</th>
<th>0</th>
<th>90</th>
<th>-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>90</td>
<td>-45</td>
<td>161.57</td>
<td>-105.26</td>
<td>164.74</td>
<td>-105.26</td>
<td>-15.26</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>-135</td>
<td>164.74</td>
<td>-105.26</td>
<td>164.74</td>
<td>-105.26</td>
<td>-15.26</td>
</tr>
<tr>
<td>3</td>
<td>62.73</td>
<td>-18.43</td>
<td>164.74</td>
<td>-105.26</td>
<td>164.74</td>
<td>-105.26</td>
<td>-15.26</td>
</tr>
</tbody>
</table>
| 3 | 51.06 | -18.43 | 164.74 | -105.26 | 164.74 | -105.26 | -15.26 | 18%
nanowire axis. The facets of the nanowire can be derived to be \{100\} by considering the twinned crystal orientation. This is similar to what was seen for the vertical nanowires in the same sample. The side facets of the Type 2 non-vertical nanowires were also examined in the samples in which the vertical nanowires showed octagonal cross-section (combination of \{100\} and \{110\}) similar to Figure 6.1 (d). It is seen that the side facets of these Type 2 non-vertical nanowires are also octagonal and similar to the vertical nanowires of the same sample. Therefore, it can be concluded that the side facets of all \(<100>\) nanowires are the same for a particular growth condition and is not affected by the 3-dimensional twinning at the bottom of the nanowire.

As the morphology of the vertical and non-vertical \(<100>\) nanowires are similar and the orientation information is lost in the transfer process to the Cu grid for TEM analysis, it is hard to be certain about the type of the \(<100>\) nanowires that were analysed under the TEM. However, while most non-vertical nanowires break above the twinned bottom region, there are few nanowires similar to the one shown in Figure 6.8 (b) that have broken off below the twinned section. These nanowires can be established to be non-vertical \(<100>\) nanowires. The crystal structure of these nanowires is also defect-free ZB once the growth in the \(<100>\) direction is initiated after the initial 3-dimensional twinning at the bottom.

For the principal sample considered, a total of 85% of the non-vertical nanowire growth directions matches with above Type 1 or Type 2 multiple-order twinning model considered up to the 3rd order. It should be noted that the remaining 15% of non-vertical nanowires represent only 1% of the entire nanowire population of the principal sample when considered with the other main types of nanowires. It should also be noted that the proportions of Type 1 and Type 2 non-vertical nanowires and even the distribution within the orders of the same type, vary with the growth conditions.

Figure 6.8: (a) A 2nd order Type 2 \(<100>\) non-vertical nanowire showing the viewing direction for the image shown in the inset. (b) Low magnification TEM micrograph of a non-vertical \(<100>\) nanowire with the twinned bottom region. (c) HRTEM image showing the ZB crystal structure above the twinned base.
The planar nanowires, the 3rd main type of nanowires grown on the (100) substrates are discussed next.

6.3.3 Planar Nanowires

Planar nanowires were studied across a number of samples, including the principal sample. For X-TEM studies, a sample with 100% planar nanowires was used due to the ease of sample preparation and analysis. 100% planar nanowire yield was achieved by pre-growth annealing the substrate at a higher temperature. The exact growth conditions will be discussed in-detail in Chapter 7.

The planar nanowires grow along the four in-plane <110> directions of the (100) substrate. As seen in Figure 6.9 (a), the tapering and the growth rate of the planar nanowires grown along the two perpendicular [011] (or [0-1-1]) and [01-1] (or [0-11]) directions are significantly different. Nanowires grown parallel to the [01-1] direction (indicated in blue in Figure 6.9 (a)) are highly tapered and have a “Christmas tree”-like shape. The growth rate of these nanowires are also lower compared to those grown parallel to the [011] direction. The
planar nanowires grown parallel to the [011] direction (indicated in red in Figure 6.9 (a)) are non-tapered. These nanowires also seem to show a preference in growing along the [01-1] and [0-11] directions compared to [011] and [0-1-1] directions. Interestingly, they can also change growth direction from one <110> direction to another by making 90° or 180° turns as indicated by the arrows in Figure 6.9 (b) and (c). A close investigation of the facets of these nanowires helps in explaining the morphology and the behaviour observed.

Figure 6.9 (d) shows an X-TEM image of a planar nanowire taken along the <011> zone axis. As can be clearly seen, the predominant growth facet of the nanowire is a {111} plane, although the resultant growth direction is <110>. This is similar to what has been previously observed for GaAs and InAs planar nanowires grown on (100) substrates [21, 22]. Therefore, in the case of planar nanowires, the growth direction is not perpendicular to the growth facet. Growth on the other facet revealed by the Au particle, i.e. the (100) facet, is very slow compared to that on the {111} plane. The base of the planar nanowires (i.e. the part that grew first) is gradually submerged with time in the 2-dimensional layer growth that simultaneously takes place on the substrate, creating an illusion as if the base of these nanowires is thinner than the tip. As seen in Figure 6.9 (e), the planar nanowires maintain the (100) top facet.

The growth of the nanowire being driven by a {111} plane explains the preference of these nanowires to grow along the [01-1] and [0-11] directions compared to [011] and [0-1-1] directions. Nanowires grown along the [01-1] and [0-11] directions are driven by (111)B polar growth facets, while those grown along the [011] and [0-1-1] directions are driven by (111)A polar growth facets. In the case of nanowires grown on (111) substrates, it is known that they generally prefer to grow along the <111>B direction (that is, driven by a (111)B facet) than along the <111>A direction (driven by a (111)A facet) [30, 31]. Similarly in this case, [01-1] (and [0-11]) oriented planar nanowires which have the (111)B facets as growth facets are dominant. However, it should be noted that the presence of some planar nanowires driven by (111)A growth facets is in contrast to what has been reported for GaAs and InAs planar nanowires [21, 22], where all nanowires were aligned parallel to [01-1], i.e. driven by (111)B facets. A similar alignment parallel to [01-1] has been observed for self-catalysed InP planar nanowires, although the exact growth facet is not explicit in this case [31]. In the current study, the (111) facet that is driving the growth of the planar nanowire can even switch between the four available {111} facets on the (100) surface, causing them to change growth direction by 90° or 180° angles. The cause of growth direction change is not completely clear. However, from careful examination of the SEM images it is clear that presence of obstacles such as other nanowires (planar, vertical and non-vertical) and uneven depositions on the substrate is one definite cause. As seen in the inset of Figure 6.9 (a), few planar nanowires may end up growing as non-vertical or even vertical nanowires, growing off the substrate during the later stage of growth.
Nanowires Grown on (100) InP Substrates: Growth Directions, Facets and Crystal Structures

The fact that the nanowires parallel to the [011] direction being grown by a (111)A facet also explains their faster axial growth rate. In the case of <111> nanowires, it has been reported that the <111>A nanowires have a higher growth rate than the <111>B nanowires [17]. Similarly in this case, the planar nanowires that are driven by (111)A facets grow faster axially. The difference in tapering and lateral growth of the two perpendicular types of nanowires could be resulting from a combination of two mechanisms. First, it has been shown that the relative lateral growth rates in the two perpendicular [011] and [01-1] directions depend on the MOVPE growth conditions [32]. At relatively low temperatures and high V/III ratios the lateral growth rate in the [011] direction is faster than [01-1] direction due to the ease of group III adatom incorporation on the group V covered [011] steps [32]. This higher lateral growth rate in the [011] direction results in larger tapering of the nanowires growing perpendicular to the [011] direction, that is, parallel to the [01-1] direction. The second mechanism involves the side facets of the planar nanowires that are shown in Figure 6.9 (e). These facets that are sloping from the top facet to the substrate are partially or fully polar similar to those discussed in the vertical nanowires, Section 6.3.1. For planar nanowires grown parallel to [01-1], the polarity of the side facets is “A”, while for nanowires grown parallel to [011], the polarity of the side facets is “B”. As discussed earlier, with the higher growth rate of A polar facets under the considered growth conditions [24-26], the side facets of the [01-1] and [0-11] planar nanowires grow faster making them more tapered and giving them the “Christmas tree”-like shape.

As seen in the TEM micrographs of Figures 6.9 (d) and (e), the planar nanowires have a defect-free ZB crystal structure, in agreement with reported GaAs and InAs [21, 22] planar nanowires. Despite being mainly grown by a \{111\} facet, the planar nanowires tend to be twin defect-free ZB due to the fact that they grow along the substrate and hence directly epitaxial to the substrate along the whole length of the nanowire. As shown in Figure 6.10 this prohibits the nucleus to take WZ or twinned positions, but to continue the stacking sequence dictated by the substrate which is defect-free ZB. 

Figure 6.10: Layer by layer stacking in planar nanowires.
99% of the nanowires on the principal sample can be explained by the three main types discussed above. Hence, considering the growth facets of these types of nanowires, it can be concluded that a vast majority of seemingly complicated nanowires grown on InP (100) substrates are actually been driven by only two kinds of facets - \{111\} and \{100\}. It should also be noted that non-vertical nanowire growth directions like \langle110\rangle\hspace{1em}\text{and}\hspace{1em}\langle112\rangle\hspace{1em} which are commonly seen on (111) and (100) substrates [12, 33-36] are not observed in this case.

### 6.4 Summary

A comprehensive study of the nanowires grown on (100) substrates was presented. The nanowires were identified to be of 3 main types; vertical, non-vertical and planar nanowires. These types of nanowires were analysed in detail in terms of morphology, growth directions, facets and crystal structure. Two kinds of non-vertical nanowires were found, and a mathematical model based on 3-dimensional multiple order twinning was presented to explain the growth directions of these two kinds of non-vertical nanowires. The experimental data obtained by measuring elevation and azimuth angles of the individual nanowires confirmed the calculated values using the model. It was found that the seemingly complex and random nanowire growth on InP (100) substrates simplifies to nanowires driven by either \{100\} or \{111\} growth facets.

Table 6.4 summarizes the growth directions, facets and crystal structure of the 3 types of nanowires discussed in this chapter.

<table>
<thead>
<tr>
<th>NW type</th>
<th>Growth direction</th>
<th>NW side facets</th>
<th>Growth facet</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Vertical</td>
<td>[100]</td>
<td>{100}, {110} or combination of the two</td>
<td>{100}</td>
<td>Planar defect free ZB</td>
</tr>
<tr>
<td>2 Non-vertical</td>
<td>\langle111\rangle after 3D multiple order twinning at the bottom</td>
<td>{112}/{-100} (same as the facets of NWs grown on (111) substrate under same conditions)</td>
<td>{111}</td>
<td>WZ with stacking faults</td>
</tr>
<tr>
<td></td>
<td>\langle100\rangle after 3D multiple order twinning at the bottom</td>
<td>{100}, {110} or combination, (same as vertical [100] NWs on the same sample)</td>
<td>{100}</td>
<td>Planar defect free ZB</td>
</tr>
<tr>
<td>3 Planar</td>
<td>Four \langle110\rangle directions</td>
<td>(100) top facet, side facets are non-uniform</td>
<td>{111}</td>
<td>Planar defect free ZB</td>
</tr>
</tbody>
</table>

**Table 6.4:** Summary of growth directions, facets and crystal structure of nanowires grown on InP (100) substrates.
The in-depth understanding presented in this chapter provides the essential grounding to control and engineer growth directions and facets of these types of nanowires grown on industry standard (100) oriented substrates for a range of new nanowire-based architectures. These aspects will be discussed in detail in the following chapter.

6.5 References


§ 6.5 References


Relative Yield Control and Side Facet Engineering of InP Nanowires Grown on InP (100) Substrates for Complex Heterostructures

Overview: In addition to being grown on industry standard orientation, the different types of nanowires grown on (100) substrates open up entirely new possibilities to grow complex structures such as nano-crosses and meshes, as well as provide new combinations of facets to engineer advanced radial heterostructures. The first part of this chapter investigates the control of the relative yields of different types of nanowires using basic growth parameters and pre-growth annealing. The second part presents the engineering of side facets of [100] oriented nanowires in order to be used as templates for complex radial heterostructures. InGaAs radial quantum wells are grown on [100] nanowires with an octagonal cross section shape in order to demonstrating this.

7.1 Introduction

All three types of nanowires discussed in Chapter 6 have been successfully demonstrated in devices, and one type or the other may be preferred depending on the targeted application or device design [1-11]. The control of different growth orientations on the same substrate could also provide options for creating new and complex structures. Non-vertical nanowire ensembles are used as strong optical scatterers [1, 2] while single non-vertical nanowires can be used as building blocks for more advanced structures such as nano-crosses, zig-zag bio-probes or even complex nanowire meshes that aims to be utilised in memory devices based on Majorana fermions [3-5, 8]. Vertical nanowires are preferred in applications where uniformity is important either in device design or fabrication steps such as in top contact formation in nanowire ensemble devices [9-11]. Planar nanowires are demonstrated in applications like transistors and can also be used as interconnects [6, 7].
Compared to the conventional (111) substrates where nanowire growth is almost always in the vertical direction, the (100) substrates provide versatility in the choice of nanowire crystallographic growth direction and their associated crystal structures [12]. However, the relative control of growth of one type over another is paramount in order to minimize device fabrication complexities as well as to increase efficiency.

Nanowire facets and cross sectional shapes are as equally important as the growth direction in many applications. Radial nanowire heterostructures are directly linked to facets that they are grown on. Uniform nanowire side facets such as \{110\} mostly yield uniform radial heterostructures [13, 14]. On the other hand, growth on facets that are non-uniform either in terms of crystal plane, polarity or dimensions can be used to create complex radial heterostructures such as twinned superlattice nanotubes, nanocavities and quantum wires [15-20].

In addition to radial heterostructures, the nanowire facets also have an influence on the optical properties of the nanowires. Different surface recombination velocities and nanoscale roughnesses of different facet types affect the carrier recombination and phonon transport in nanowires [21-23]. The nanowire cross section shape, which is determined by the type of facets and their relative dimensions, is important in applications where the nanowire is used as an optical cavity, as it can affect the types and number of modes that are confined [24]. Furthermore, nanowire facets can be used as alternative templates to patterned substrates in order to grow quantum wires and wells, thereby eliminating the need for complex processing and patterning. Mimicking of A-ridge quantum wires would be one such example [20].

Further to being grown on the industry standard substrate orientation and being defect-free ZB, \(<100>\) nanowires open up a completely new family of available facets, their combinations and resulting cross section shapes [25] such as square and octagonal shapes, that are almost unobtainable with nanowires grown in other orientations. Some of these shapes and combinations are given in Table 6.1 in Chapter 6. The combinations comprise of symmetric, asymmetric, non-polar and partially polar facet combinations that are not well studied so far, yet could open up many possibilities in terms of applications of nanowire facets discussed above.

This chapter demonstrates the control of relative yields of different types and facets of nanowires grown on the (100) substrates. Pre-growth annealing conditions and basic growth parameters are tuned in order to achieve high yields of each type of nanowires. Next, the facets of the \(<100>\) oriented nanowires are engineered to achieve most of the profiles discussed in Table 6.1, while maximising the vertical yield. Two techniques, namely TMIn flow rate variation during growth and \textit{in-situ} post growth annealing are used in order to
achieve this. Finally, an application of one of the asymmetric facet profiles is demonstrated by growing InGaAs radial QWs on them. The complex nature of QW growth on different facets and resulting optical properties are studied.

### 7.2 Experimental Methods

All nanowires discussed in this chapter were grown on InP (100) substrates seeded by colloidal Au particles. 30 nm diameter seed particles were used for the study of relative yields, while 30 and 50 nm particles were used for the facet engineering study. Again, 50 nm Au particles were used for the core nanowire growth of QWT structures. A range of growth parameters have been investigated in this chapter. Most growth series discussed in Sections 7.1 – 7.3 are centred around a standard sample whose growth parameters are given in Table 7.1. Some other series are also discussed and the specific details of those growth conditions are given under each section. Specific details of radial QW growth are also provided in Section 7.7.

The samples were investigated using SEM, TEM and PL measurements. X-TEM samples of the nanowires in the initial stages of growth were prepared by tripod polishing and the lateral cross sections of the nanowires were prepared by microtome sectioning. For the single nanowire PL measurements, the nanowires were transferred to a sapphire substrate by sonication and drop cast method due to the ease of achieving a well separated even distribution of single nanowires using this technique. For the ensemble measurements, the nanowires were transferred by gently rubbing the two surfaces. EDX analysis was carried out within the TEM system using 0.5 or 0.7 nm spot size.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-growth annealing temperature</td>
<td>450°C</td>
</tr>
<tr>
<td>PH$_3$ flow during the annealing step</td>
<td>8.93 × 10$^{-4}$ mol/min</td>
</tr>
<tr>
<td>Pre-growth annealing time</td>
<td>10 min</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>450°C</td>
</tr>
<tr>
<td>V/III ratio</td>
<td>350</td>
</tr>
<tr>
<td>TMIn flow for the nanowire growth</td>
<td>2.015 × 10$^{-6}$ mol/min</td>
</tr>
<tr>
<td>Growth time</td>
<td>1 hr</td>
</tr>
</tbody>
</table>

**Table 7.1:** Pre-growth annealing and growth parameters of the standard sample.
7.3 Variation of Relative Yields with Basic Growth Parameters

In this section, the effect of growth temperature, V/III precursor ratio and the TMIn flow rate on the relative yields has been studied and all samples discussed in this section have been annealed prior to growth under conditions similar to the standard sample unless specified otherwise. For this study, the Type 1 and Type 2 non-vertical nanowires discussed in the previous chapter are considered together.

7.3.1 Effect of Growth Temperature

The growth temperature of the nanowires was varied between 425 and 500°C around the standard sample while keeping the other parameters the same. Figure 7.1 (a) shows the effect of the growth temperature on the relative yields of the 3 different types of nanowires. The
Figure 7.2: (a) Dependence of the relative yields of the different types of nanowires on the (a) V/III ratio. (b) TMIn flow.

temperature range of 450 – 475°C is favourable for the vertical nanowire growth. However, as seen in the Figure 7.1 (c) and (d) when grown at 475°C, the top parts of most nanowires are kinked to a <111> direction by forming one (or an odd number) of 3 dimensional twins. Further experiments carried out by varying growth time reveal that this change of growth direction takes place during cooling down by precipitating InP from the In that was left in the Au particle and also possibly the growth chamber. Surface energy change due to In depletion from the particle may have caused the twin formation and the change of growth direction as shown in [26]. This effect was not seen at 450°C (Figure 7.1 (b)) and lower temperatures, and hence lowering the temperature to 450°C before switching off TMIn could prevent the kinking as shown in Figure 7.1 (e).

Even though the vertical yields of growths done at 450°C and 475°C are similar, a slight increase of temperature to 500°C drastically changes the nanowire growth on (100) substrates. As shown in Figure 7.1 (f), at 500°C, the nanowires do not nucleate. Instead, deposition of material seems to take place around the particle, using it as a nucleation site. It should be noted that this is distinctly different from planar nanowires which have clear growth orientations and are driven by the Au particle.

In addition, the non-vertical nanowire yield increases with decreasing growth temperature.

7.3.2 Effect of V/III Ratio and TMIn Flow Rate

V/III ratio was varied around the standard sample from 220 to 700 for this study by varying only the PH₃ flow. Its effect on the relative yields is shown in Figure 7.2 (a). A moderate V/III ratio of 350 promotes vertical nanowire growth and higher or lower values seem to be
unfavourable for the vertical nanowires. There is also no clear correlation between the V/III ratio and the other two types of nanowires.

For the study of the effect of TMIn flow rate, both, group III and group V flow rates were varied together, so that the V/III ratio remains constant along the series. As the TMIn flow rate is directly related to the growth rate of the nanowires, the growth time of these growths has also been scaled accordingly. The pre-growth annealing temperature used for this series (shown in Figure 7.2 (b)) is slightly different to the standard sample. These samples were annealed at 390°C instead at 450°C. However, it is seen that there is a general trend of increasing non-vertical yield with the increasing TMIn flow rate irrespective of the pre-growth annealing condition. This takes place at the expense of decreasing vertical yield.

Overall, it is seen that the relative yields are highly sensitive to the growth conditions. For example, as seen in Figure 7.1, a 25°C decrease in nanowire growth temperature from 450 to 425°C can drastically alter relative yields by causing the vertical yield to drop from 76% to 17% and non-vertical yield to increase from 20% to 65%. An increase of 25°C in growth temperature from 475 to 500°C could prevent nucleation of nanowires entirely.

A similar study on the effect of growth parameters has been carried out by Wang et al. [27]. It should be noted that no pre-growth treatment has been carried out in that study, and the “missing” nanowires in the patterns and the planar nanowires in the current study could be of same origin. The trends seen are broadly similar, especially in terms of temperature and V/III ratio. The contrasts observed in terms of the exact V/III values and trend with the variation of TMIn flow rate could be due to differences in the reactor itself and reactor
related parameters such as the pressure and the total flow. The Au particle deposition technique and arrangement could also be playing a role.

§ 7.4 Effect of Pre-Growth Annealing Conditions on the Relative Yields

In this section, the effect of the pre-growth annealing temperature and PH$_3$ flow rate during annealing on the relative yields are studied. Most series are grown centered around the same standard sample discussed above. All nanowires are grown at 450°C with a TMIn flow rate of $2.015 \times 10^{-6}$ mol/min and V/III ratio of 350 subsequent to pre-growth annealing.

7.4.1 Effect of Pre-Growth Annealing Temperature

The samples are annealed at temperatures between 360 and 600°C before nanowire growth, which was carried out under identical conditions. It could be seen from Figure 7.3 that the vertical nanowire yield shows a strong dependence on this parameter. Rather low pre-growth annealing temperatures promote vertical nanowire growth on InP (100).

7.4.2 Effect of PH$_3$ Flow Rate During Pre-Growth Annealing

PH$_3$ over pressure is very commonly used during the annealing step in order to prevent the substrate from decomposing. Here, it is found that this flow rate of PH$_3$ also has an effect on the subsequent yields of nanowires. For this experiment the effect of PH$_3$ flow rate is examined across three different annealing temperatures that were studied in the previous section. Figure 7.4 (a-c) shows the variation in relative yields with the PH$_3$ flow rate for pre-growth annealing temperatures of 390, 450 and 600°C, respectively.

Compared to 450°C and 600°C, there is not much variation in yields with the PH$_3$ flow rate at the temperature of 390°C. This could be due to the very low decomposition of PH$_3$ at

Figure 7.4: Variation of relative yields of the different types of nanowires with the PH$_3$ flow rate during pre-growth annealing at (a) 390°C, (b) 450°C, (c) 600°C.
that low temperature [28, 29], which makes the yields indifferent to the variations in the PH₃ flow rate. This observation also indicates that it is P or a partially decomposed product of PH₃, that is affecting the relative yields and not PH₃ itself. At higher pre-growth annealing temperatures, the increased PH₃ flow rate leads to an increased yield of planar nanowires.

Combining the above observations and those from other samples grown (not shown), it could be concluded that the vertical growth of nanowires is highly sensitive to the pre-growth annealing condition of the Au seed particles as well as the growth parameters of the nanowires. Nanowire growth in this otherwise energetically unfavourable direction does not allow for a large growth parameter window. Pre-growth annealing under a relatively low temperature promotes subsequent vertical growth of nanowires. Growth temperatures between 450 °C and 475 °C and V/III ratios in the range of 350 are favourable for vertical nanowires. The trimethylindium (TMIn) precursor flow rate should also be low. 87% vertical nanowires are achieved by pre-growth annealing at 390 °C under a PH₃ flow rate of 4.46 × 10⁻⁴ mol/min and then carrying out the growth at 450 °C and V/III ratio of 350.

Non-vertical nanowire growth mainly depends on the flow rate of TMIn during nanowire growth, although low growth temperature also seems to promote non-vertical nanowire growth. 67% non-vertical nanowires are achieved by using a high flow rate of TMIn at 4.030 × 10⁻⁵ mol/min.

Planar nanowire growth is highly sensitive to the pre-growth annealing condition. High pre-growth annealing temperature and high PH₃ flow rate during annealing promotes formation of planar nanowires. 100% planar nanowires can be achieved for the same nanowire growth condition as the above vertical nanowires, by simply annealing the sample at 600 °C under high PH₃ flow rate of 2.23 × 10⁻³ mol/min.

The pre-growth annealing and growth conditions for high yields of each type of nanowires are summarised in Table 7.2.

<table>
<thead>
<tr>
<th>NW Type</th>
<th>Pre-growth annealing condition</th>
<th>Growth parameters</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
<td>PH₃ flow (mol/min)</td>
<td>Temperature</td>
</tr>
<tr>
<td>1 Vertical</td>
<td>390 °C</td>
<td>4.46 × 10⁻⁴</td>
<td>450°C</td>
</tr>
<tr>
<td>2 Non-vertical</td>
<td>390 °C</td>
<td>8.93 × 10⁻⁴</td>
<td>450°C</td>
</tr>
<tr>
<td>3 Planar</td>
<td>600 °C</td>
<td>2.23 × 10⁻³</td>
<td>450°C</td>
</tr>
</tbody>
</table>

**Table 7.2:** Summary of pre-growth annealing conditions and growth parameters to achieve high yields of different types of nanowires.


7.5 Initial Stages of Formation of Different Types of Nanowires

As shown previously, the formation of the different types of nanowires depends on a number of parameters. The exact link between the parameters that were previously investigated and the growth mechanisms are not clear at this stage. Wang et al. have shown that the vertical and non-vertical growth directions are governed by the liquid-vapour interface energy which is strongly dependent on the In concentration in the Au particle [26]. Consequently, relatively lower In concentrations in the particle leads to <111> non-vertical growth, whereas higher In concentrations show preferential <100> growth [26]. This may explain the kink seen during the cooling down stage in the nanowires grown at 475°C (shown in Figure 7.1 (c) and (d)) in the current study. Yet, it does not explain the observation of increased non-vertical nanowire yield with the increasing TMIn flow rate discussed in Section 7.3.2., which is contrary to this argument.

In order to gain more insight into the effect of growth conditions on the type of nanowires grown, the initial stages of formation of the 3 different types of nanowires have been studied here. For the vertical and planar nanowires, the growth was carried out for a few seconds under pre-growth and growth conditions that yielded 85% and 100%, respectively. In the case of non-vertical nanowires, the sample discussed in Figures 7.1 (c) and (d) was used due to the ease of analysis. Nanowires of the same sample that were at different stages of kinking were analysed.

The evolution of the 3 types of nanowires from nucleation to early growth stages is shown in a series of X-TEM images in Figure 7.5. Comparing the particles shown in Figure 7.5 (a)i and (b)i, that have only been annealed, it is clear that the different pre-growth annealing treatment has affected the nano-particle differently. The particle collects In from the substrate and forms an alloy during pre-growth annealing. Comparing the sizes of the particles along the evolution, it is also clear that the particle absorbs more In during the initial stages of growth. Hence, as discussed earlier, the In percentage in the particle could be playing a role in determining the growth direction. It should be noted that pre-growth annealing at lower temperature (390°C), which should incorporate less In, has resulted in higher vertical yield in the present case. Again, this observation is not in complete agreement with ref [26], which reported a relatively high In concentration leading to high vertical yield.

Careful examination of the Au particle – substrate/nanowire interface during the early stages of growth (series (a)-(c) in Figure 7.5) also reveals that the combination of facets that are wetted by the Au particle are different in each series and that they dynamically change before selection of the final growth direction. In most cases, the particle wets multiple facets that are in competition before the final growth direction is established. Theoretical models by
Relative Yield Control and Side Facet Engineering of InP Nanowires
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Schwarz and Tersoff [30, 31] have shown that the different growth directions may arise from interplay between facet growth and introduction of new facets at the growth front as well as droplet statics. They have also shown that different growth modes can be stable under the same growth conditions, and the actual growth mode is decided by the initial conditions such as annealing and patterning, [31] which is similar to the current case of planar and vertical nanowire growth. This is due to the new facets formation during the complex transient state before a steady state is established, [31, 32] which is also evident in present experimental results.

Although the kinked nanowires shown in Figure 7.5 series (c) do not correspond directly to the growth conditions used in the sample with a high non-vertical yield in Table 7.2, it gives an understanding of the process of 3-dimensional twin formation and changes in the position of the Au particle that vary with the external In supply. Group III flow rate (or

**Figure 7.5:** X-TEM images of; (a)i a Au particle that has been annealed under conditions which yield 100% planar nanowires and then cooled down before initiating growth (0 s growth), (a)(ii-v) stages of evolution of growth of planar nanowires, growth has been carried out for 8 s in (ii) and 30 s in (iii-v). (b)i a Au particle annealed under conditions that yield 85% vertical nanowires – 0 s growth (6 such particles were examined in order to eliminate statistical effects), (b)(ii-v) stages of evolution of vertical nanowires, growth has been carried out for 12 s in (ii) & (iii) and 30 s in (iv) & (v). (c)(i-v) TEM images of stages of 3D twin formation and growth in non-vertical directions. Few different stages of growth could be captured in series (a)-(c) by analysing the same sample due to slight differences in growth rates and delays in nucleation between the individual nanowires. All micrographs are imaged along <011> zone axis. Scale bars in series (a) and (b) are 10 nm and 50 nm in series (c).
§ 7.6 Engineering the Side Facets of <100> Oriented Nanowires

Group III partial pressure) has been shown to affect the surface energies as well as chemical potential of the nano-particle [30, 33]. In the current study, the growth is further complicated by the presence of multiple growth facets in the initial stage of growth, which could eventually lead to tilting and 3-dimensional twin formation. More detailed quantitative modelling of the complex initial conditions is required in order to fully understand the effect of these pre-growth annealing and growth conditions on the resulting nanowire type.

7.6 Engineering the Side Facets of <100> Oriented Nanowires

As seen in Chapter 6.3.1 (see Table 6.1), <100> oriented nanowires present a new family of facets over conventional <111> nanowires side facets shown in Table 2.1. These facets can be engineered not only for novel and complex radial heterostructures, but also for controlling optical properties as discussed in Section 7.1. This section presents engineering of these facets to achieve most of the profiles listed in Table 6.1, while controlling yield for vertical nanowires. Vertical nanowires are preferred for many ensemble applications [9-11] and in this case, also bring the advantage of ease of analysis with SEM and TEM.

From the growths carried out in the previous section, it is seen that the nanowire facets do not depend on the pre-growth conditions, but only on the growth conditions. The distinct side facets of nanowires evolve mainly with lateral growth. In addition, surface diffusion and surface evaporation could also contribute to this [34, 35]. These factors are limited by the kinetics and thermodynamics that are governed by the growth parameters during growth. Indeed, as shown in Chapter 6.3.1, for vertical nanowires, the facets just below the particle form an octagonal shape, which is the polygon shape made up of low index facets that is closest to a circular shape. This in-turn allows the particle to remain close to a spherical shape with minimum distortion and surface energy [26, 36]. As shown in 6.3.1, this octagonal shape soon evolves into a distinct cross section shape dictated by the growth conditions within about 200 nm. The discussion in the current section concentrates only on the evolved, stable cross section shape, which accounts for a large portion of the nanowires.

Figure 7.6 shows the facet variation of the <100> oriented nanowires with the growth parameters discussed in Section 7.3. The schematic of the profile is also shown for clarity. In addition to those presented in Section 7.3, 420°C is also included in the temperature series in order to highlight the rapid change in facet profiles with temperature. For the growth temperature of 475°C, the facets of the vertical [100] oriented segment are examined by focusing on the lower non-kinked part of the nanowire.
Relative Yield Control and Side Facet Engineering of InP Nanowires Grown on InP (100) Substrates for Complex Heterostructures

The temperature variation from 420 to 450 °C has drastically changed the facets from four {011} facets to four {100} facets via octagonal shape comprising of both types of facets. Considering the similar nanowire heights of 1 μm, it should be noted that there is no significant difference in the tapering from 420 to 450 °C. The trend significantly changes at the growth temperature of 475 °C. Again, the height of the <100> segment of these nanowires is 1 μm, which allows direct comparison of lateral growth by comparing the cross sectional area. The lateral growth in the [01-1] and [0-11] directions is very small, although there is not much difference in the lateral growth in the [011] and [0-1-1] directions compared to lower growth temperatures. The side view of the nanowires (not shown) reveals that most nanowires are thinned at the base. This suggests that some surface decomposition and evaporation take place at 475 °C. It should also be noted that these <100> nanowires are much more prone to thermal decomposition. In a separate experiment, it was seen that all 30 nm <100> nanowires were completely decomposed in the process of temperature ramping from 450 to 650 °C, even under PH₃ overpressure, while the <111> WZ nanowires still

**Figure 7.6:** Variation of the side facets of the <100> oriented nanowires with the basic growth parameters. Series, (a) temperature, (b) V/III ratio, (c) TMIn flow. All scale bars are 100 nm.

<table>
<thead>
<tr>
<th>Temperature:</th>
<th>420 °C</th>
<th>425 °C</th>
<th>450 °C</th>
<th>475 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="a" alt="Facets" />i</td>
<td><img src="a" alt="Facets" />ii</td>
<td><img src="a" alt="Facets" />iii</td>
<td><img src="a" alt="Facets" />iv</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>V/III ratio:</th>
<th>200</th>
<th>350</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="b" alt="Facets" />i</td>
<td><img src="b" alt="Facets" />ii</td>
<td><img src="b" alt="Facets" />iii</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TMIn flow (mol/min):</th>
<th>2.015 × 10⁻⁶</th>
<th>2.418 × 10⁻⁵</th>
<th>4.03 × 10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="c" alt="Facets" />i</td>
<td><img src="c" alt="Facets" />ii</td>
<td><img src="c" alt="Facets" />iii</td>
<td></td>
</tr>
</tbody>
</table>
survived. Here, a similar, lower level of decomposition could be competing with the also slow lateral growth that takes place under low TMIn flow rate.

As discussed in Chapter 6.3.1, the inclined \{011\} facets show partial polarity. It has been shown that, P-terminated B polar InP surfaces decompose much faster than A polar surfaces due to the two unpaired electrons associated with the P atoms \([37, 38]\). Although the bonds are not exactly similar in the current case of partial polarity, similar trends in reactivity can be expected due to higher fraction of P atoms on tilted (01-1) and (0-11) facets. This would lead to more competition from decomposition on the (01-1) and (0-11) facets compared to (011) and (0-1-1) facets, leading to lesser lateral growth in the former facets compared to lower growth temperatures where decomposition was not present. This results in the highly elongated shape observed at 475°C growth temperature.

Recalling the discussion of Chapter 6.3.1, the V/III ratio should play a role in the resulting cross section shape with high V/III ratio promoting the faster over growth of partially A polar, tilted (011) and (0-1-1) facets and hence, enhancing the asymmetry in the two perpendicular <011> directions. However, no such asymmetry is observed in the V/III range that is studied here. One reason for this is, the complete range experimented (200 to 700) being relatively high in terms of V/III ratios generally used in MOVPE. Therefore, no obvious differences are seen from SEM analysis. Also, as shown in Chapter 6.3.1, such asymmetries are overgrown within a couple of hundred nanometres. Hence, after 1 μm of growth, they are not visible along bulk of the nanowire, of which the more prominent facets are symmetric {100} facets.

Increase in TMIn flow rate (and hence the growth rate) results in facet change from \{100\} to \{011\}. Considering the longer length of the nanowires grown with higher TMIn flow rates, the tapering parameters\(^8\) are actually decreasing with increasing flow rate, although the absolute lateral growth increases as seen in series (c) in Figure 7.6. The facets seen for the highest TMIn flow rate studied (4.030 × 10\(^{-5}\) mol/min) are most interesting. The cross section shape is roughly octagonal, yet it does not comprise of low surface energy and/or low index facets. The facets are further complicated by the irregular micro-facets seen along the facet (see 45° titled view in Figure 7.6 (c) iii). Further study is required in order to understand the formation of these facets.

In the following two sub-sections, two methods, namely, TMIn flow rate variation and \textit{in-situ} post growth annealing are used to achieve most of the facet profiles discussed in Table 6.1, while maximising the yield of vertical nanowires.

\(^8\) Tapering parameter is calculated as, (average NW width at the base – hemispherical NP diameter)/(2 × average NW length)
Relative Yield Control and Side Facet Engineering of InP Nanowires
Grown on InP (100) Substrates for Complex Heterostructures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMIn pre-flow time</td>
<td>15 s</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>450°C</td>
</tr>
<tr>
<td>V/III ratio</td>
<td>309</td>
</tr>
<tr>
<td>TMIn flow rate for the nanowire growth</td>
<td>$1.619 \times 10^{-5}$ mol/min</td>
</tr>
<tr>
<td>Growth time</td>
<td>30 min</td>
</tr>
</tbody>
</table>

Table 7.3: Pre-growth and growth parameters for high vertical yield nanowires with \{011\} facets.

7.6.1 Facet Engineering by TMIn Flow Rate Variation

In the previous section, it was shown that for <100> oriented nanowires, lower growth temperatures and higher TMIn flow rates promote \{011\} type side facet formation with the possibility of accessing facet profiles in between \{011\} and \{100\} for intermediate parameters. Yet, in both cases, these growth parameters result in a large decrease in the vertical yield. The high vertical yield growth conditions discussed so far always resulted in \{100\} type facets, with the exception of growth at 475°C, which presented other complications.

Another method of achieving high vertical yield [100] nanowires by pre-filling the Au particles with In (as opposed to pre-growth annealing method discussed here), has been demonstrated by Wang et al. [26]. The TMIn molar fraction used in that study was quite high and close to that which resulted in \{011\} side-facets in Figure 7.6 (c)ii [26, 39].

In the current study, this technique which has been demonstrated for patterned substrates, has been reproduced for nanowires seeded by colloidal Au particles. 50 nm Au particles were used for this study, and similar pre-growth and growth parameters to ref [26] (including molar fractions) were used as given in Table 7.3.

As shown in Figure 7.7 (a) and (b), these growth conditions yielded ~ 65 - 80% vertical nanowires with <100> oriented nanowires having \{011\} side facets as expected. It should be noted that similar growth conditions have resulted in \{100\} type side facets in the original study by Wang et al. [26, 27] and this could be due to subtle differences such as reactor configuration and total flow.

The TMIn flow rate could be further increased by three times without compromising the vertical yield (~72%). In this case, the particle pre-filling time was reduced by 3 times in order to keep the In percentage in the particle almost the same at the time of nucleation. The facets of the resulting nanowires shown in Figure 7.7 (e) are similar to those previously seen for very high TMIn flow rate in Figure 7.6 (c)iii. In the following section, these facets are further engineered to form low index combinations by in situ post growth annealing.
7.6.2 Facet Engineering by in-situ Post Growth Annealing

The stability of facet profiles in nanowires is determined by the surface energy and surface-to-volume ratio [25]. The surface energy is mainly decided by the type of facet, for example {011} type facets have lower surface energy compared to {100} facets [40, 41]. The surface-to-volume ratio, which is equal to circumference-to-area ratio (assuming constant nanowire height), is governed by the cross section shape; an octagonal cross section has a lower ratio compared to a square cross section. Annealing could provide thermal energy to overcome the kinetic energy barrier for the surface migration of atoms [34], resulting in a facet profile that would minimise the total surface related energy with the optimum balance between the facet types and cross sectional shape.

The amount of thermal energy that is supplied can be controlled by two annealing parameters, namely temperature and time. These will in-turn control the volume of material that is migrated and the distance the atoms could migrate, and hence the resulting facet profiles of the nanowires.

In the previous sections {100}, {011} and high index facet profiles were achieved. In this section, these nanowires are used to achieve profiles in between {100} and {011}, such as octagonal and elongated octagonal cross sectional shapes. As stated in Section 7.6, <100> nanowires cannot withstand high annealing temperatures, limiting the parameter range in terms of annealing temperatures. Hence, annealing time is used in this study in order to engineer nanowire facets. Annealing was carried out directly after growth at 550°C for durations between 20 s and 10 min under PH₃ overpressure. It should be noted that surface migration also takes place during the temperature ramp up interval from 450°C growth temperature to 550°C annealing temperature.

Figure 7.7: (a) 45° tilted SEM view of nanowires grown using the TMIn pre-flow technique. (b) Top view of nanowires shown in (a). (c) Schematic showing the facet profile and the directions with respect to the substrate in (b). (d) 45° tilted SEM view of nanowires grown using TMIn pre-flow techniques and 3 times higher flow. (e) Top view of a nanowire from (d).
### Table 7.4: Summary of pre-growth, growth and post growth anneal parameters in order to achieve different facet profiles while maintaining high vertical yield.

<table>
<thead>
<tr>
<th>Facet combination</th>
<th>Cross sectional geometry</th>
<th>Pre-growth &amp; growth parameters</th>
<th>SEM</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Four {100} facets</td>
<td>Square</td>
<td>Pre-growth annealing 390°C</td>
<td><img src="image1.png" alt="" /></td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PH&lt;sub&gt;3&lt;/sub&gt; flow rate during annealing Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Growth temperature 450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 350</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Four {110} facets</td>
<td>Square</td>
<td>Could not be obtained, as vertical growth requires high V/III ratio</td>
<td><img src="image2.png" alt="" /></td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>Rectangular</td>
<td>TMIn pre-flow time 15 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Growth temperature 450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 309</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Combination of {100} and {110}</td>
<td>Perfect octagonal</td>
<td>TMIn pre-flow time 5 s</td>
<td><img src="image3.png" alt="" /></td>
<td>III</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature 450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 309</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate Very High</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-growth anneal 10 min @ 550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Elongated octagonal</td>
<td>TMIn pre-flow time 15 s</td>
<td><img src="image4.png" alt="" /></td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature 450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 309</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate High</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-growth anneal 20 s @ 550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>OR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn pre-flow time 5 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature 450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 309</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate Very High</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-growth anneal 210 s @ 550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexagonal</td>
<td>Pre-growth annealing 450°C</td>
<td><img src="image5.png" alt="" /></td>
<td>V</td>
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<tr>
<td></td>
<td></td>
<td>PH&lt;sub&gt;3&lt;/sub&gt; flow rate during annealing Medium</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Growth temperature 475°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V/III ratio 350</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMIn flow rate Low</td>
<td></td>
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</tbody>
</table>

Note: Most nanowires contain a short kinked segment on top.
7.7 Growth of Complex Radial Heterostructures on the Facets of [100] Oriented Nanowires

In this section, an In$_x$Ga$_{1-x}$As QW is grown on a Type IV facet profile (see Table 7.4), that is achieved using the first technique of 20 s post growth annealing. This profile was selected as it gives access to three different types of facets (\{100\}, tilted \{011\} partially A polar and...
tilted \{011\} partially B polar facets) with three different lengths, demonstrating radial heterostructure growth on anisotropic facets. As will be discussed later, the behaviour of this chosen structure is somewhat similar to QW growth on \Lambda-ridges [42, 43]. In fact, these nanowires present the possibility to grow quantum wells and wires similar to those grown on ridges and grooves which are well known to be highly efficient [42-45] on nanowires, with the added advantages of very low device foot print, transferability to foreign substrates and, easy and better control of dimensions by control of facet widths.

The In\textsubscript{0.35}Ga\textsubscript{0.65}As QW and barriers were grown at 550°C after annealing for 20s. A nominally 6 nm thick InP lateral layer was grown on the nanowires before QW growth in order to ensure a high quality interface for the QW. The TMIn to TMGa ratio in vapour for the QW growth was 29:71 with flow rates of $6.746 \times 10^{-6}$ and $1.653 \times 10^{-5}$ mol/min, respectively. The V/III ratio used for the QW growth was 115 and the QW growth was carried out for 35 s. Another InP layer was grown as the second barrier of the QW for 8 min with expected nominal thickness of 24 nm. As even the shortest facets (\{100\} facets in this case), are well formed with a lengths of over 30 nm, the structures grown on all facets will be forming quantum wells as opposed to wires [20, 42] (also see Figure 7.9 (c)).

Figure 7.9 (a) and (c) show an SEM image and a bright field X-TEM image of the complete structure, respectively. One very distinct observation is the difference between the QW thicknesses on the three types of facets. QWs on the \{100\} facets are much thicker than those on the \{011\} facets. Of the QWs on \{011\} facets, those on the (011) and (0-1-1) facets are thicker than QWs on (0-11) and (01-1) facets. The QWs on the (0-11) and (01-1) are almost non-existent in thickness and it is seen that the InP outer barrier layer growth on these facets is also very thin in most nanowires. In addition to the \{100\} facet, two \{013\} facets (marked by yellow arrows in Figure 7.9 (c) and (d)), form the inner interface of the \{100\} QW. These are somewhat similar to the \{311\}A facets formed in the [01-1] oriented V-groove and ridge quantum wires [46-49].

The compositions of the QWs on the \{100\}, \{011\} and (0-1-1) type facets were examined. A sample in which the QW material (with same composition) was grown much thicker was used for this purpose in order to overcome the limitation of the probe size in EDX measurements and avoid contribution from the InP barriers. Assuming that there is no variation in the composition with the QW thickness, the composition of the QWs on \{100\} facets is found to be In\textsubscript{0.35}Ga\textsubscript{0.65}As, with the In percentage being about 6% higher than that in vapour during growth. This is similar to what was observed for WZ phase \{1-100\} facets in [111] nanowires in Chapter 4. Interestingly the composition on the (011) and (0-1-1) facets was In\textsubscript{0.42}Ga\textsubscript{0.58}As, even higher in In composition. The composition of the (0-11) and (0-11) facets could not be measured as their thicknesses were still too low even when grown for a
§ 7.7 Growth of Complex Radial Heterostructures on the Facets of [100] Oriented Nanowires

The differences in QW thickness are mainly due to the different growth rates on different facets. InGaAs, especially Ga-rich InGaAs grows faster on {100} facets compared to {011} facets under similar conditions to those used for the QW growth in this study [50, 51]. The asymmetry between the thickness of two perpendicular {011} type facets are due to the opposite partial polarities that arise with tapering which was discussed in Chapter 6.3.1 [12, 50, 52, 53]. In addition, factors such as capillarity arising from the lengths of the facets and angles between them, strain due to lattice mismatch and entropy of mixing could play a role in altering the chemical potential of the facets [44, 45, 54, 55]. The differences in the surface chemical potential could cause a surface flux of adatoms around the nanowire from longer time.
one facet to another (perpendicular to the growth direction) resulting in changing growth rates \([44, 45, 54, 55]\) and hence the thicknesses of the QWs. However, these effects are very small compared to the variation in simple material growth rate on the different facet orientations.

The effect of capillarity is relatively more significant in altering the composition of the facets. The \(\{100\}\) facets are much shorter than the other two facets and hence the curvature (or the sharpness) is higher around these facets compared to the \(\{011\}\) facets. This results in higher chemical potential on the \(\{100\}\) facets, arising solely from shape \([44, 45, 55]\). Hence, during growth, the adatoms that have higher relative mobility, which is In in the current case, diffuse away from this higher potential facet much easier than Ga which has lower relative mobility \([44, 45, 55]\). This results in higher In compositions on \(\{011\}\) facets and relatively higher Ga compositions on \(\{100\}\) facets. Similar observations have been made in the case of InGaAs and other ternary shells grown on [111] oriented nanowires with hexagonal cross sections, where bands rich in lower mobility group III element had formed along the corners of the apices \([56, 57]\). The above segregation is controlled by the entropy of mixing effect, which increases the chemical potential on the \(\{100\}\) facets for Ga and decreases that for In \([45]\). However, the segregation effect is further enhanced by the stress field built up by the strain \([54]\), which favours more In adatom diffusion towards already In rich and less strained \(\{011\}\) facets.

In addition to the above effects, differences in absorption, decomposition and desorption of the metalorganic precursors on different facets also play a role in determining the facets thickness as well as their relative compositions \([58-62]\). The final resulting thickness and the composition are decided by the combination of all these effects discussed above.

Figure 7.10 (a) shows the room temperature PL spectrum from a representative single QWT nanowire dispersed on a sapphire substrate. The QWs are bright and efficient with the InP nanowire core emission barely visible as shown in the inset. Only a single emission peak is visible from the QWT at room temperature. The average thicknesses of the \(\{100\}\) and \(\{011\}\) (and \(0-1-1\)) QWs were measured using X-TEM images. They were \(4.63 \pm 0.53\) and \(0.96 \pm 0.43\) nm, respectively. The thickness of the \(\{011\}\) and \(0-1-1\) QWs were difficult to be accurately measured due to the contrast variations at the interfaces stemming from high strain. The thickness of the \(01-1\) and \(0-11\) was sub-nanometre and was also not able to be measured within reasonable accuracy. However, by comparing with the calculated emission wavelengths for thicknesses in the \(\pm 1\) nm range of the measured value of \(\text{In}_{0.35}\text{Ga}_{0.65}\text{As}\) and \(\text{In}_{0.42}\text{Ga}_{0.58}\text{As}\) QWs (grey and red shaded regions shown in Figure 7.10 (b)), it is clear that the observed emission could only be from the \(\text{In}_{0.35}\text{Ga}_{0.65}\text{As} \{100\}\) QWs. The calculations done
Figure 7.10: (a) Room temperature PL spectrum from a representative single nanowire QWT. The inset shows the zoomed-in view of the 800-1050 nm region showing the faint InP emission. (b) Expected room temperature emission wavelengths calculated using the $8 \times 8$ k-p model for different well thickness of compositions $\text{In}_{0.35}\text{Ga}_{0.65}\text{As}$ and $\text{In}_{0.42}\text{Ga}_{0.58}\text{As}$. The two red and grey shaded areas roughly mark the ±1 nm region around the average well thicknesses measured by TEM. (c) PL spectra from a representative nanowire ensemble measured at 77 K, the inset shows the zoomed-in view of the 800-1050 nm region where a peak at 953 nm is visible in addition to the InP peak at 877 nm. (d) Calculated emission wavelengths for different QW thicknesses of $\text{In}_{0.35}\text{Ga}_{0.65}\text{As}$ at 77 K. The inset shows the calculated emission wavelengths for very thin $\text{In}_{0.42}\text{Ga}_{0.58}\text{As}$ QWs from 0.85 to 1.2 nm at 77 K.

Using the eight-band k-p model suggests a thickness of around 5.25 nm corresponding to the observed wavelength, which is slightly thicker than the measured $4.6 \pm 0.53$ nm. This slight discrepancy could be due to factors such as variation in composition along the nanowire.

Figure 7.10 (c) shows a representative spectrum of a nanowire ensemble measured at 77 K. Again, the InP nanowire core/barrier is only faintly visible. However, more importantly, another peak around 953 nm is observed in this case. Figure 7.10 (d) shows the
calculated emission wavelengths for In$_{0.35}$Ga$_{0.65}$As and In$_{0.42}$Ga$_{0.58}$As QWs at 77 K. The main peak matches with ~6 nm thick In$_{0.35}$Ga$_{0.65}$As QW, confirming that the main peak is again pertinent to the QW on {100} facets. The expected emission wavelength for In$_{0.42}$Ga$_{0.58}$As QWs with thicknesses around 1 nm is in the vicinity of the observed peak wavelength of 953 nm. It is also fair to assume that carriers have sufficient thermal energy and are not confined in the very thin sub-nanometre (0-11) and (01-1) QWs, even at 77 K. In addition, as mentioned earlier, and as seen in some nanowires examined by X-TEM, the barrier growth on these two facets can also be too thin to confine carriers, making them less likely candidates to be attributed to the emission observed at 953 nm. Therefore, within experimental errors, it could be concluded that this peak is related to carrier recombination in the (011) and (0-1-1) QWs. The high brightness and efficiency seen in {100} QWs and, very low InP core emission could be due to these higher energy {011} QWs efficiently trapping and transporting carriers into the lower energy {100} QWs [63, 64], avoiding recombination elsewhere.

7.8 Summary

In summary, this chapter demonstrated the development of the nanowires that were fundamentally studied in Chapter 6 into ‘application ready’ and tuneable building blocks. The relative yields of different types of nanowires were controlled by varying the pre-growth annealing conditions and growth parameters. Low pre-growth annealing temperature and precursor flow rates were preferred by vertical nanowires, while non-vertical nanowires preferred a high precursor flow rate. Planar nanowires were achieved by increasing the pre-growth annealing temperature and PH$_3$ flow rate during this step. Maximum yields of 87%, 67% and 100% were achieved for vertical, non-vertical and planar nanowires, respectively.

In addition to growth directions, facets of the <100> oriented nanowires were also engineered to obtain a variety of facet combinations resulting in cross sectional shapes from square to octagonal. This was achieved while maintaining a high yield of vertical nanowires. Nanowire facets were solely dependent on the growth parameters and it was seen that slow growth rates resulted in {100} type facets, while fast growth rates mostly yielded {011} facets. Facets were further engineered by post growth in situ annealing to form octagonal and elongated octagonal cross section shapes comprising of a combination of {011} and {100} facets. Finally, InGaAs QWs were grown on nanowires with asymmetric {100}-{011} facet combination, demonstrating the usability of these novel facet combinations for complex structures. The control of yield and facets demonstrated here, should increase the interest in these nanowires grown on the industry standard (100) oriented substrates in a wide range of novel applications that are based on complex nanowire architectures.
7.9 References


Relative Yield Control and Side Facet Engineering of InP Nanowires Grown on InP (100) Substrates for Complex Heterostructures


Relative Yield Control and Side Facet Engineering of InP Nanowires Grown on InP (100) Substrates for Complex Heterostructures


[54]. Q. Xie, A. Madhukar, P. Chen and N. P. Kobayashi, "Vertically Self-Organized InAs Quantum Box Islands on GaAs(100)," *Physical Review Letters*, vol. 75, no. 13, pp 2542-2545, 1995.


Relative Yield Control and Side Facet Engineering of InP Nanowires Grown on InP (100) Substrates for Complex Heterostructures
Conclusions and Future Research Directions

8.1 Conclusions

This thesis explored new directions in terms of growth of InP nanowires and related heterostructures, for the next generation of nanowire devices that could be seamlessly integrated with micro-electronics and other planar devices on a single chip. It presented a gradual progression from investigating unexplored areas of heterostructure growth on conventional InP (111) substrates to means of transferring the current knowledge of growth on InP (111) substrates to Si (111) substrates. The work was further extended to change the conventional nanowire growth direction to the industry standard [100] orientation.

The first experimental chapter (Chapter 4), investigated InP-InGaAs heterostructures grown on InP nanowires, a material combination highly used in planar heterostructures, but unexplored in their nanowire-based counterpart. As the material combination is most commonly used in optical communications related applications in its planar form, here too, QW structures emitting in the 1.3 μm communication wavelength region were grown. Uniform QW growth around the InP nanowire cores was achieved and they displayed efficient recombination at the QW with bright emission at room temperature. Some similarities with the planar heterostructures, such as different levels of interface diffusion between the two interfaces, were found. One main difference in the nanowire InGaAs QWs and the planar QWs was the material phase. The nanowire QWs were grown on WZ phase m-plane and hence the WZ InGaAs QWs on m-plane WZ InP were modelled using the 8×8 k·p model. The growth evolution of the QWs with growth time was studied in detail and was used to achieve tunability in the interested wavelength region by varying the QW thickness. Composition variation was also used to demonstrate tunability in the 1.3 μm wavelength region, showcasing the versatility of this material system in the nanowire form. Finally, MQW structures with even brighter emission were successfully grown by extending the SQW structure. This work certainly draws attention to this material combination which is less studied in nanowire form, by demonstrating its potential for quantum heterostructures.
The need for the InP nanowires to be grown on Si in order to be integrated with the mature micro-electronics technology, was addressed by replicating the well-studied growth on InP (111)B substrates, on a thin buffer layer that was optimised on Si (111) (Chapter 5). The buffer layers were grown in two steps and the growth conditions for each step were optimised in order to achieve a smooth epitaxial InP surface that completely covered the underlying Si substrate. The choice of very low growth temperature during the first step, gave rise to self-catalysed whisker growth that had to be suppressed by optimising the V/III value to be extremely high. The final buffer layer seemed to have fully relaxed during the second stage of growth relieving any residual strain from the initial layer growth. Twin formation was observed both parallel and inclined to the substrate. Twin density parallel to the substrate was high at the interface, but had greatly reduced with increasing thickness during the second layer growth. Some of the inclined twins had propagated through to the surface, yet, it was found that these did not affect the subsequent growth of nanowires. Most importantly, the buffer layer grown on non-polar Si substrates was found to be of P-terminated (111)B polarity without any anti-phase domains, which was ideal for vertical nanowire growth by VLS mechanism. The yield of vertical nanowires on the buffer layer was 97%. Nanowires were grown on InP (111)B substrates and the buffer layer under the same conditions for comparison. It was found that they had similar morphological, structural and optical properties demonstrating the ability to directly use the same growth parameters that are well studied and used for the growth on InP (111)B substrates. Hence, this approach can easily be used even to grow complex heterostructures similar to those discussed before, on Si substrates. In addition, the formation of a barrier between the Si substrate and Au particles used as seeds for the nanowires is another major advantage.

The ultimate requirement in terms of substrates for the future nanowire devices would be to grow on Si (100) substrates. However, almost no work has been done on vertical III-V nanowire growth on Si(100) substrates and knowledge on vertical homoepitaxial growth is also limited to a few publications [1-5]. In this work, considerable effort has been made to understand nanowire growth on (100) oriented substrates, mainly by studying the homoepitaxial growth on InP (100) substrates, so that it builds up the knowledge base required to achieve the ultimate goal of growing vertical nanowires on Si (100) substrates.

Vertical nanowire growth on [100] oriented substrates is challenging, as it is not the natural, energetically favourable direction for the growth of nanowires. The resulting growths are seemingly complex and lacking in uniformity of growth direction. This complexity was carefully analysed and a thorough study was presented in terms of growth directions, facets and crystal structures in Chapter 6. The seemingly random nanowires were found to be <100>, <111>B and <011> oriented nanowires that inherited various growth directions with respect to the substrate in the first two cases, due to three dimensional
§ 8.1 Conclusions

twinning that took place at the bottom of the nanowires. The possible growth directions for these nanowires, with respect to the substrate were calculated using a mathematical model, which was confirmed by angles measured experimentally on single nanowires. The nanowire facets and the crystal structures were common for a particular growth orientation irrespective of the three dimensional twinning that took place during the initial stages. The $<100>$ nanowires shared the octagonal cross-section shape comprising of four $\{011\}$ and $\{100\}$ facets close to the Au particle, which soon evolved into a shape that is dictated by the growth conditions. The $<111>$ nanowires showed the same facets as those seen on the vertical nanowires on the InP (111)B substrates. In both these cases, the growth facet between the nanowire and the Au particle was perpendicular to the growth direction, forming $\{100\}$ and $\{111\}$ growth facets, respectively. However, the $\{011\}$ oriented planar nanowires were revealed to have $\{111\}$ growth facets that are inclined to the growth direction. The crystal structures of the $<100>$-, $<111>$ and $<011>$ nanowires were twin defect-free ZB, WZ with stacking faults and twin defect-free ZB, respectively. The planar defect formation was governed by the freedom each new bilayer has in terms of choosing its nucleation position. The crystal phase and the defect density in the case of $<111>$ nanowires were governed by the growth conditions and was the same as that of the InP (111)B control sample.

This detailed study and understanding of the structural aspects of nanowires grown on (100) substrates formed the basis to further control and engineer growth directions and facets, in order to be used in novel applications (Chapter 7). The vertical, non-vertical and planar nanowire yields depended on growth parameters as well as pre-growth annealing conditions and these were optimised for each category to yield maxima of 87% vertical, 67% non-vertical and 100% planar nanowires. Complete understanding of each type’s relationship with the growth condition requires further work. However, preliminary work indicated that the facet growth, introduction of new facets at the growth front and In concentration in the Au particle, which in turn affect the surface energies and chemical potential could have a combinational effect.

The novel $<100>$ growth orientation opens up completely new combinations of side facets and cross-sectional shapes, and it was found that the formation of a certain facet profile depended only on the growth parameters and not on pre-growth annealing conditions. However, they could be further engineered by post-growth in situ annealing. Therefore, by using the right combinations of growth and post–growth annealing conditions, a range of facet profiles with cross-section shapes ranging from square to octagonal was achieved, while maintaining a high yield of vertical nanowires. The potential of asymmetric nanowire side facets was demonstrated by growing InGaAs QWs on them. It was seen that the thickness as well as the composition on different types of facets were different; showing interesting optical properties different to those studied previously on [111] oriented nanowires. The work presented in this dissertation on nanowire growth on (100) substrates,
not only proved that nanowire growth on (100) substrate is interesting and vertical growth is possible, but also that it has potential to facilitate novel structures that were inaccessible through conventional [111] oriented nanowires.

8.2 Future Research Directions

Numerous advancements have been demonstrated in this thesis, in terms of growth of InP nanowires and related heterostructures, aiming for future optoelectronic device applications. The work presented, especially the growth of nanowires on (100) substrates, also opens up many unexplored opportunities as well as some unanswered questions. Three main areas of future work have been identified based on the work presented in Chapters 4 to 7.

8.2.1 Theoretical Modelling and Understanding of the Vertical Nanowire Nucleation on (100) Substrates

As discussed in Section 7.5, the growth direction of nanowires on (100) substrates seems to depend on both the In concentration in the Au particle as well as dynamic facet formation and facet growth. Close inspection of the early stages of vertical nanowire formation reveals an interesting evolution of facets as shown in Figure 8.1. The Au particle, which is initially submerged in the substrate, gradually rises with deposition on the sub-surface interfaces. Yet, the shape of the particle is largely retained as seen in Figure 8.1 (c). Either by VLS mechanism or by accumulation of material, depositions are formed as marked by yellow arrows in Figure 8.1 (c) and (d) at the periphery of the particle, almost guiding the particle upwards. In fact, the deceptive highly tapered shape seen in the [100] nanowires at the initial stages (see Figure 8.1 (e)) are actually these growths that took place before the Au particle fully emerged from the substrate.

Figure 8.1: (a) Top view SEM image of 30 nm Au particles annealed under the conditions that yield 85% vertical nanowires and then cooled before initiating growth. (b) X-TEM image of (a). (c)–(f) Stages of evolution of vertical nanowires after 12 and 30 s of growth. Red dashed line in (c) and (d) indicate the interface between Au particle and substrate/nanowire and yellow arrows indicate the growths that take place at the periphery of the particle. All X-TEM images are taken in <011> zone axis. The scale bar in (a) is 100 nm and 10 nm in (b)-(e).
The fundamental understanding of this unprecedented evolution is important not only to bridge the knowledge gap in the area of vertical nanowire growth on (100) substrates, but also to achieve vertical nanowire growth on other (100) substrates like GaAs, GaP and InAs. Theoretical modelling of the nucleation stages using classical nucleation theory could therefore be useful in this regard.

8.2.2 Investigating Other Complex Heterostructures Grown on [100] Oriented Nanowires and Their Applications

Chapter 7 demonstrated means of achieving different facet profiles on [100] oriented nanowires and complex heterostructures that can be grown on them. The knowledge gained in Chapters 6 and 7 on the radial growth of [100] nanowire facets and the demonstrated different facet profiles can be used in combination to accomplish many other interesting configurations of heterostructures.

For example, for the radial heterostructure demonstrated in Chapter 7.7, the {100} facets were formed during the temperature ramp up and annealing steps, and during the InGaAs shell growth, the {100} facets grew faster as they do under high precursor flows (see Sections 7.6 and 7.7). Now, one could avoid the {100} facet formation by eliminating temperature ramp up and annealing steps and growing the InGaAs shell at the same temperature as the core growth temperature (450 °C). If the InGaAs growth is carried out under high flow, {100} facet growth rate should be faster resulting in growth of quantum wires that runs along the edges of the nanowire as shown in Figure 8.2 (a). These could show very interesting magneto-PL properties [6] and would be a good alternative for the popular V-groove architecture with orders of magnitude smaller footprint, high and easily controllable device density and easy fabrication that does not involve etching or processing steps. These can even be further extended to stack multiple coupled wires as shown in Figure 8.2 (b).

Similarly, the converse is also possible by using the square cross-sectioned {100} faceted nanowires. If high flow rates are again used to grow the InGaAs QWs, {100} facets will grow faster, separating the tube like structure into four planar QWs at the corners, as shown in Figure 8.2 (c). This will allow the design and fabrication of four-sided devices on the side facets of the nanowires [7].
Figure 8.2: (a) Quantum wires grown at the corners of the [100] nanowires with {011} facets. (b) Cascaded multiple quantum wires. (c) Separated shell growth on {100} facets, a X-TEM image of a such sample is shown aligned to the schematic, the InGaAs layers are marked in yellow for clarity in the X-TEM image. (d) Nano-cavity formation by selective etching. (e) Nano-wall formation by selective etching.

As mentioned above quantum wire structures can be used just like the V-groove structures for lasers and light emitting diodes with suitable device design [8, 9]. In addition to quantum structures, by use of materials that can be selectively etched against InP, cavities and other interesting configurations such as the ones shown in Figure 8.2 (d) and (e), can be achieved. In the latter case, once the etching process is optimised, this can be used to achieve smaller spacing and dimensions that are not accessible by selective area growth or top down approach. The cavities in Figure 8.2 (d) can be functionalised with metal particles [10] or colloidal quantum dots for photonic devices, whereas structures like those shown in Figure 8.2 (e) can be used as well-aligned nano-walls and fins that are increasingly gaining attention as alternative geometries to planar structures and nanowires [11-13].

The above examples only considered radial heterostructures. By combining also with possible axial heterostructures of different materials, there are countless opportunities to develop heterostructures for novel devices on industry standard (100) oriented substrates.
8.2.3 High Vertical Yield InP Nanowire Growth on Si (100) Substrates

The ultimate goal in integrating nanowire devices with Si technology would be to grow them on Si (100) substrate as it is the industry standard substrate and orientation. Since [100] InP nanowires demonstrated in this work are seeded with Au particles, direct growth on Si (100) would not be an option. Hence, the intermediate thin buffer layer approach will have to be adopted. As the same growth parameters discussed in Chapters 6 and 7 can now be used for the growth of nanowires on the buffer layer, it will eliminate the additional efforts that would have been required to explore the growth parameters for vertical nanowire growth on Si (100).

However, the challenge here would be achieving a smooth buffer layer while it is still thin (~ <150 nm). It is known that III-V layer growth on Si (100) is rougher than that on Si (111) substrates [14], and smoothness in the reported layers that were primarily grown for planar structures, were achieved only after few microns of growth [15-17]. If the maximum benefits are to be reaped from the nanowire growth on a buffer layer, the layer thickness needs to be kept to a minimum, thereby reducing the costs and growth time (while providing a smooth surface for the vertical nanowire growth). These aspects could form a basis for future research.

Finally, it can be seen that progress made in this research in terms of InP nanowire growth aiming for future optoelectronic devices show great promise for a number of meaningful new research areas as well as for improvement of existing nanowire devices to achieve even better outcomes.

8.3 References

Conclusions and Future Research Directions


