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***Quantum Dots Engineering in III-V
Nanowires for Applications in Photonics***

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Abstract

Semiconductor quantum dots (QDs) have emerged over the past decade as a pivotal solid-state platform for on-demand quantum light sources, fundamental for a wide range of quantum technology applications. In particular, QDs emitting within the telecommunication bands (1.3 – 1.55 μm) are of great interest for quantum communication, as this wavelength range coincides with the low-loss window of standard optical fibers, essential for long-distance quantum signal transmission. Among the different material platforms explored so far, $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP nanowires (NW-QDs) stand out as a promising platform, offering precise control over QD size, composition, and density within a scalable growth scheme. Although many milestones have been demonstrated in these NW-QDs, key challenges remain, most notably maintaining crystal phase purity and source brightness when extending QD emission into the telecom range. In conventional wurtzite (WZ) InP NWs grown along the $\langle 0001 \rangle$ direction, the achievable crystal phase purity is limited by the catalyst diameter, which in turn constrains the QD geometry and emission wavelength flexibility.

In this thesis, these challenges are addressed through the investigation of $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP NWs grown along the $\langle 100 \rangle$ direction, characterized by a zincblende (ZB) crystal phase. The ZB structure is intrinsically less sensitive to stacking faults formation, allowing greater flexibility in achieving defect-free QDs of larger planar dimensions and tunable emission across the telecom bands. Using Chemical Beam Epitaxy (CBE), the growth parameters are optimized to obtain straight, phase-pure $\text{InAs}_x\text{P}_{1-x}/\text{InP}$ heterostructure NWs and realizing QDs with emission tunable up to the third telecom window. Furthermore, an in-situ grown, monolithic waveguide was developed solely through vapor–liquid–solid (VLS) growth, guided by finite-difference time-domain (FDTD) simulations. The optimized geometry leads to a significant enhancement of the photon extraction efficiency, experimentally confirmed by an order-of-magnitude increase in photoluminescence intensity.

Additionally, this work explores the control of crystal phase purity in conventional WZ InP/InAs_xP_{1-x} NWs grown along the <0001> direction. It will be demonstrated that the ternary alloy composition plays a key role in stabilizing the crystal phase, with pure-phase WZ structures achieved by tuning the As content. The phenomenon is investigated both experimentally and theoretically. These findings provide a viable route to overcome the well-known diameter-dependent phase purity limitation, extending the design space for WZ NW-QDs emitters.

Overall, the results presented in this thesis establish ZB InAs_xP_{1-x} NW-QDs as a flexible and efficient platform for telecom-compatible light sources. The demonstrated control over crystal structure, emission wavelength, and integrated waveguide geometry represents a significant step forward toward scalable, fiber-coupled single-photon emitters for next-generation quantum communication technologies.

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List of Publications

1. **G. Bucci**, V. Zannier, F. Rossi, A. Musiał, J. Boniecki, G. Sęk, and L. Sorba, “Zincblende InAs_xP_{1-x}/InP Quantum Dot Nanowires for Telecom Wavelength Emission”, *ACS Appl. Mater. Interfaces*, 2024, 16, 20, 26491-26499, DOI:[10.1021/acsami.4c00615](https://doi.org/10.1021/acsami.4c00615)
2. **G. Bucci**, V. G. Dubrovskii, V. Zannier, F. Beltram, and L. Sorba, “The role of composition and diameter in the crystal purity of InAs_xP_{1-x} nanowires”, *Nanoscale*, 2025, 17, 19939-19945, DOI: [10.1039/D5NR02409A](https://doi.org/10.1039/D5NR02409A)
3. **G. Bucci**, T. Gzyl, A. Musiał, V. Zannier, F. Beltram, W. Rudno-Rudziński, G. Sęk, and L. Sorba, “Enhanced Photon Extraction through Optimized Waveguide Geometry for Zincblende InAsP/InP Nanowire Quantum Dots Emitting in Telecom Range”, accepted in *ACS Appl. Nano Mater.*, 2026, DOI: [10.1021/acsanm.5c04842](https://doi.org/10.1021/acsanm.5c04842)
4. R. A. Sorodoc, P. De Vincenzi, A. S. Sharma, **G. Bucci**, M. Roggi, E. Mugnaioli, L. Sorba, M. De Luca, and V. Zannier, “Tunable GaAs_xP_{1-x} Quantum-Dot Emission in Wurtzite GaP Nanowires”, *ACS Appl. Mater. Interfaces*, 2024, 16, 47, 65222-65232, DOI:[10.1021/acsami.4c15343](https://doi.org/10.1021/acsami.4c15343)
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6. A. Lombardi, G. Shukla, **G. Bucci**, S. Salimian, V. Zannier, S. Traverso, S. Fracassi, N. Traverso Ziani, M. Sassetti, M. Carrega, F. Beltram, L. Sorba, and S. Heun, “Supercurrent modulation in InSb nanoflag-based Josephson junctions by scanning gate microscopy”, accepted by *Nat. Comm. Mat.*, DOI: [10.48550/arXiv.2506.15342](https://doi.org/10.48550/arXiv.2506.15342)

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Chapter 1: Introduction

1.1 Background

Over the past decade, quantum technologies have become a central focus of both scientific research and technological innovation. Quantum systems can exploit superposition, entanglement, and quantum interference to perform tasks that are extremely challenging for classical devices, enabling secure communication, quantum computation, and quantum-enhanced sensing - all of which are expected to revolutionize key sectors of science and industry¹⁻⁷. Among the various hardware platforms currently investigated, photonic approaches have shown particular promise for applications involving long-distance data transmission, such as global quantum networks, quantum key distribution, and distributed quantum computing. In this framework, semiconductor quantum dots (QDs) have emerged as a pivotal solid-state platform for the realization of on-demand quantum light sources suitable for quantum technologies^{1,8-12}. Semiconductor QDs can be grown with a high degree of tunability using mature epitaxial techniques, offering compatibility with existing optoelectronic and photonic integration technologies. Due to three-dimensional quantum confinement, QDs exhibit discrete atom-like energy levels, making them ideal candidates for deterministic single-photon and entangled photon emission. Their emission wavelength can be engineered through composition, size and strain, allowing operation in technologically relevant spectral ranges, including telecom bands (1.3 μm - 1.55 μm). Recently, the realization of QDs in III-V semiconductor nanowires (NWs) has attracted increasing attention due to their scalability¹³. NW-based architectures provide additional control over the QD morphology and composition, enabling site-controlled growth and efficient light extraction. In particular, recent progress in InAsP/InP NW-QDs system has demonstrated single photon emission within the telecom O- and C-bands, representing a crucial step toward long-distance, fiber-based quantum networks^{10,14,15}. The convergence of precise nanoscale growth control, flexible heterostructure engineering, and integration with photonic

circuits make III-V semiconductor NW-QDs as a key technological platform in the emerging landscape of quantum technologies. Despite remarkable achievements, several challenges remain, including the control of the QD crystal quality environment, the realization of stable emission within the telecom bands, and precise control in the epitaxial growth of such structures. Addressing these issues is essential for realizing practical and scalable quantum information systems based on semiconductor nanostructures.

1.2 Scope and outline of this thesis

This thesis aims to advance the state of the art in the realization of telecom-band emitting semiconductor QDs, with a particular focus on $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP NWs. The challenges previously mentioned are addressed by changing the NW growth direction from the typically explored $\langle 0001 \rangle$ to $\langle 100 \rangle$, which allows the formation of a phase-stable ZB crystal nanostructures. InP ZB NWs can be grown with larger catalyst diameters without defects, reducing the QD aspect ratio and possibly giving higher brightness in the telecom bands compared to the WZ counterpart. Furthermore, the ZB electronic parameters are well-characterized, providing a reliable link between experimental data and theoretical modelling. The $\langle 100 \rangle$ growth direction, however, has not been previously explored for such heterostructures, and its realization introduces new challenges in engineering QDs with tailored geometries, fine-tuning of the QD features, and avoiding kinking in the NW. Chapter 2 discusses and deepens the state of the art, providing the proper background for the results discussed in the following chapters. Chapter 3 provides a detailed overview of the experimental methods employed in this work. Chapter 4 focuses on the optimization of the growth protocols to achieve controlled QDs, presenting the challenges encountered, the strategies developed to overcome them, and demonstrating tunability of the emission into the telecom bands. Chapter 5 addresses the design and growth of NW-based waveguides, exploring how radial and axial growth conditions can be tuned to enhance photon extraction efficiency at telecom wavelengths. Chapter 6 investigates an alternative solution to a major challenge in $\langle 0001 \rangle$ WZ NW-QDs, namely the suppression of stacking faults in the QD environment, which limits

device performances, exploiting the $\text{InAs}_x\text{P}_{1-x}$ ternary alloy. Chapter 4, 5 and 6 leads to publications, Ref.16, Ref.17 and Ref.18, respectively.

In addition to the main focus of this work, the PhD research included two side projects. The first involves the realization of QDs in the $\text{GaAs}_x\text{P}_{1-x}/\text{GaP}$ material system, enabling emission in the NIR region. This work has been published¹⁹ and is presented in the appendix A1. Another side project concerns the growth on InSb nanoflags and their application in devices with Josephsons junctions, which resulted in two publications^{20,21} but are not discussed in this thesis.

Finally, Chapter 7 summarizes the main results achieved and outlines perspectives for future research.

Chapter 2: State of the Art

Introduction

In this chapter, the state of the art and the framework of this thesis are provided. In Section 2.1, an overview about the III-V semiconductor NWs is discussed, which are the main nanostructures investigated during the thesis. Section 2.2 is focused on deepens the state of the art of semiconductor QDs devoted to telecom emission, highlighting the main achievements and challenges present in the literature.

2.1 III-V semiconductor NWs

Semiconductor nanostructures characterized by reduced dimensionality have represented one of the most active and rapidly advancing fields of materials science over the past decades, providing both profound physical insights and groundbreaking technological developments. Among these, III-V compound semiconductors play a central role thanks to their superior optical and electronic properties, which make them ideal for applications in optoelectronics and advanced photonics^{22–25}. The reduction of III-V semiconductors to the nanoscale further unlocks additional opportunities enabled by quantum confinement²⁶. In this thesis, we focus on semiconductor nanowires (NWs), a prominent example of such structures²⁷. NWs are quasi-one-dimensional structures with diameters typically ranging from 10 to 100 nm and lengths up to several micrometres. Their needle-like morphology induces strong carrier confinement in the radial direction²⁸, while charge carriers remain free to move along the axial direction. Owing to these features, III-V NWs have been extensively investigated over the last decades and have demonstrated outstanding optical and electronic performances^{29–31}, due to their tunable and typically direct band gaps, high carrier mobility, and large absorption coefficients. Many

applications have been reported in photonics, electronics, energy, biology, and for magnetic devices³². NWs can be fabricated using two general approaches: *top-down*, based on lithography and etching, and *bottom-up*, based on epitaxial growth or, even though they will not be deepened in this thesis, other solution-based approaches³³. The top-down route is highly scalable, but its drawbacks include: (i) a restriction to the availability of bulk materials, (ii) dimensions limited by lithography resolution, and (iii) surface roughness resulting from etching, which deteriorates electronic and optical properties^{34–36}. For these reasons, research has largely focused on the *bottom-up* approach, which is also the focus of this thesis. In particular, epitaxial growth of NWs provides precise control over their final structural and compositional properties, also enabling unique advantages. First, by selecting suitable substrate orientations and growth conditions, it is possible to control the crystal phase of the NWs. While bulk III-V semiconductors generally crystallize in the cubic zincblende (ZB) phase (except nitrides), NWs can also stabilize the hexagonal wurtzite (WZ) phase, which exhibits distinct and technologically interesting electronic properties. This aspect will be discussed in detail in subsection 2.1.2. Another crucial advantage of NWs is their ability to realize heterostructures without generating misfit dislocations. In fact, in conventional 2D epitaxial growth, lattice mismatch between two materials often results in strain relaxation through the formation of dislocations (misfit or threading) at the interface^{37–39}, or even results in 3D islands nucleation (Stranski-Krastanov growth mode)^{40–42}. In contrast, due to their high aspect ratio, NWs can efficiently relax strain elastically in the radial direction^{43,44}, enabling the integration of highly lattice-mismatched materials in a dislocation-free manner. This feature is particularly relevant for the material systems investigated in this work. In the core part of this thesis, we focus on InAs-InP NW heterostructures (and their ternary alloys), which exhibit a high lattice mismatch of $\sim 3.2\%$ ^{45,46}. Such a mismatch makes planar heteroepitaxy extremely challenging⁴⁷, although strategies such as the use of metamorphic buffer layers have been explored to improve crystal quality^{48,49}. NWs, however, allow the direct realization of InAs-InP interfaces by appropriately tuning the growth conditions. In the appendix, there is also a report on GaAs-GaP NW heterostructure, which present an even larger lattice mismatch of $\sim 3.7\%$ ⁴⁶.

The remainder of this section is dedicated to the epitaxial growth methods and mechanisms of III-V NWs (subsection 2.1.1), which constitute the core techniques employed in this thesis. I will also provide an overview of the crystal structures accessible in NWs (subsection 2.1.2) and discuss the main challenges associated with the growth of NW heterostructures (subsection 2.1.3), thereby establishing the background necessary for the results presented in the following chapters.

2.1.1 Epitaxial growth of III-V semiconductor NWs

The bottom-up growth of III-V semiconductor NWs can be achieved either by employing a catalyst seed to promote oriented growth or by a catalyst-free approach. The latter, typically referred to as *selective area epitaxy* (SAE), relies on the use of an inert dielectric mask (commonly SiO₂ or SiN) patterned with nanoscale holes defined by lithographic techniques (Figure 2.1.1.1 (a)). NWs selectively nucleate and grow within these holes, where the growth substrate surface is exposed to the precursors fluxes. The NW position and diameter are consequently primarily determined by the hole position and lateral dimensions. Although SAE provides precise control of NW positioning, lithographic techniques is intrinsically limited in resolution, thus restricting the achievable range of NW diameters. In contrast, much of the development of NWs has been driven by metal catalyst-seeded growth, particularly through the *vapor-liquid-solid* (VLS) mechanism. This process was first reported by Wagner and Ellis at the Bell Laboratories⁵⁰ in the 1960s for micrometer-scale Si NWs, and was rapidly extended to nanometer-diameter NWs and compound semiconductors in subsequent years. In the VLS mechanism, a metal nanoparticle (NP) acts as a catalyst, forming an eutectic alloy with one or both elements of the target NW material. Upon annealing, the NP becomes liquid once the eutectic temperature is reached – typically lower than the melting point of the pure constituents. When precursors are supplied, semiconductor atoms dissolve into the droplet until supersaturation occurs, leading to precipitation at the liquid-solid interface beneath the NP and driving oriented crystal growth. If radial growth is negligible, the resulting NW inherits the diameter and the position of the catalyst particle. Furthermore, the NW

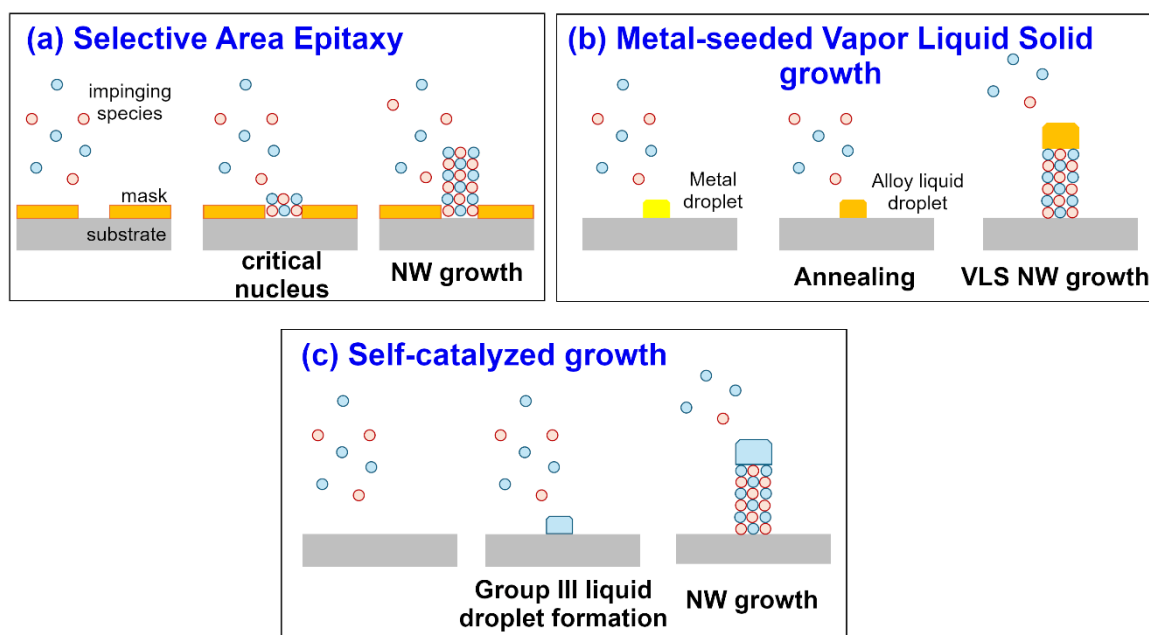


Figure 2.1.1.1 Schematic of typical methods to epitaxially grow NWs: (a) with selective area epitaxy (SAE); (b) metal-seeded vapor-liquid-solid (VLS) growth, and (c) self-catalyzed NW growth.

material will be determined by the precursors provided in the growth chamber, with the possibility to also realize ternary alloys. A schematic of the VLS process is shown in Figure 2.1.1.1 (b). It is worth mentioning that in some cases the catalyst NP seems to remain solid during growth, leading to a *vapor-solid-solid* (VSS) process, which has the major advantage of enabling fast switching of materials in axial NW heterostructures^{51,52}. Gold (Au) is the most widely used catalyst, but other metals, such as Ag^{53,54}, Cu⁵⁵, Sn⁵⁶, and Ni⁵⁷ have also been successfully employed⁵⁸. For applications in which a possible contamination of metal from the catalyst in the NW is problematic, *self-catalyzed growth* has been developed (Figure 2.1.1.1 (c)), where group III droplets (Ga or In) themselves serve as a catalyst. This approach has attracted considerable attention due to its high potential, but it also poses challenges, particularly in controlling NW diameter^{59,60}. In this thesis, I mainly focus on Au-catalyzed growth, while further details on self-catalyzed NWs can be found in Refs. 61–64. Different strategies exist for defining the metal catalyst NPs. The simplest is the use of colloidal Au nanoparticles, commercially available with diameters ranging from ten to hundreds of nanometers. Another common route is the dewetting of thin Au films deposited on the growth substrate by thermal evaporation. Upon annealing, the film splits up into droplets whose size and density depend critically on the initial film thickness, annealing conditions, and duration⁶⁵. This method produces ensembles of NWs with broad diameter distributions, and it is suitable for applications where NWs with different lengths and diameters are required in the same sample.

Alternatively, lithographically defined Au disks offer much greater control, allowing both the position and size of the NWs to be predetermined^{66,67}, which is particularly promising for scalable integration. However, this approach remains limited by lithographic resolution and disk thickness control during the metal deposition, since the final NP catalyst volume depends on both the disk thickness and lateral dimensions.

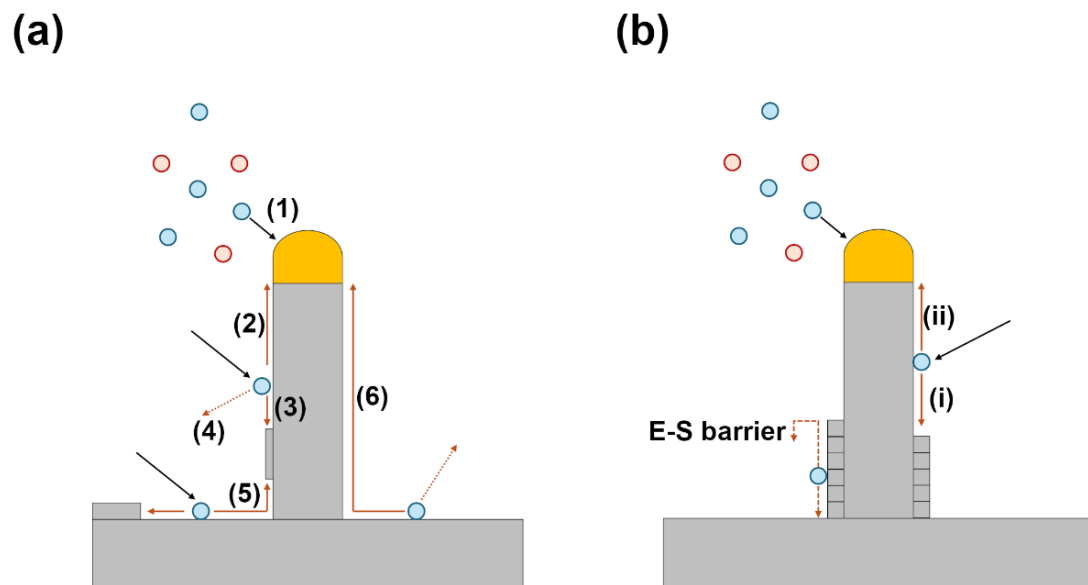
While the schematic in Figure 2.1.1.1(b) provides a simple picture of VLS growth, the actual growth dynamic of a NW is more complex since several diffusion pathways are involved. At the typical III-V NW growth temperatures (280-500°C, depending on the material), group III adatoms exhibit diffusion lengths of several micrometers, while group V species generally have much lower diffusivity and mainly contribute through direct impingement onto the catalyst droplet⁶¹. Therefore, growth involves not only direct incorporation into the catalyst but also diffusion processes of the group III adatoms. A more comprehensive picture of the NW growth is shown in Figure 2.1.1.2 (a). The main material transport pathways are:

- *Direct impingement on the catalyst:* group III and V atoms incorporate directly into the droplet and drive axial growth via VLS (process (1) in Figure 2.1.1.2 (a)). Re-evaporation from the droplet surface of the material may also occur.
- *Impingement and adatom diffusion on the NW sidewalls:* group III adatoms landing on the NW sidewalls can diffuse to the droplet (process (2) in Figure 2.1.1.2 (a)) contributing to axial growth, or nucleate directly on the sidewalls, driving radial growth of the NW (process (3) in Figure 2.1.1.2 (a)). Re-evaporation (process (4) in Figure 2.1.1.2 (a)) can occur from certain facets (i.e. {110} facets in InP NWs grown along the <100> direction⁶⁸). Sidewall impinging fluxes are also influenced by the NW density due to the existence of shadowing effects between NWs.
- *Diffusion of adatoms from the substrate:* group III adatoms on the substrate can migrate toward the NW base and, subsequently, contribute to either radial (process (5) in Figure 2.1.1.2 (a)) or axial growth of the NW (process (6) in Figure 2.1.1.2 (a)). When the NW-to-NW distance is comparable to the diffusion length of group III adatoms on the substrate, competition effects between neighbouring NWs arise and influence the growth⁶⁹.

The interplay of all these processes results in a complex balance between thermodynamics (e.g., nucleation at the droplet interface) and kinetics (e.g., diffusion and incorporation pathways). Several growth regimes have been identified⁶¹, depending on the relative importance of these mechanisms for certain material systems, diameters, and growth techniques.

Besides axial elongation, NWs often exhibit simultaneous radial growth, leading to tapering or more complex NW morphologies. Understanding and modelling this growth mechanism is non-trivial, as it depends sensitively on growth conditions and the competition between sidewall crystal nucleation and axial incorporation through VLS. One class of models describes radial growth in NWs through mass-transport balance, where sidewall nucleation competes with axial growth due to the group III adatom diffusion process⁷⁰. These models explain tapering and enhancement of radial growth at lower temperatures⁷¹. Key parameters include the effective diffusion length of group III adatoms (λ_{III}) on the NW sidewalls, which, in turn, depends on growth temperature, V/III ratio, facet type and polarity, and NW diameter, with enhanced radial growth for larger facet surfaces⁷². However, such models cannot account for abrupt radius changes observed experimentally, such as “pencil-shaped” NW morphologies. For this reason, more refined descriptions invoke a *step-flow mechanism* for radial growth^{73–76}. The

Figure 2.1.1.2: (a) Kinetic pathways of the adatoms transport during the growth of the NW: (1) direct impingement, (2) diffusion from the sidewalls, (3) diffusion from the sidewalls for the radial growth, (5) diffusion from the substrate for the radial growth, (6) diffusion from the substrate for the axial growth; (b) schematic of the step-flow mechanism for the NW radial growth



mechanism is schematized in Figure 2.1.1.2 (b): sidewalls grow layer-by-layer, analogous to conventional 2D epitaxy. If an adatom impinges on the NW sidewalls, it has a certain probability to diffuse to the catalyst droplet (process (ii) in the figure). Once adatoms impinge beyond the effective diffusion capture zone of the droplet on the NW sidewalls, they form 2D islands on the NW sidewalls. Additional adatoms preferentially attach to existing step edges (process (i) in the figure), rather than nucleating new islands, leading to layer completion. Successive layers then form, yielding radial thickening of the NW. An *Ehrlich-Schwoebel* (E-S) *barrier* is typically assumed, reflecting the hindrance of downward adatom diffusion from upper layers at step edges^{77,78}. Due to the complexity of the involved parameters, quantitative modelling often requires numerical simulations. Overall, two main regimes are generally distinguished: (i) a first *pure axial growth regime* when NW length is shorter than the adatom diffusion length λ_{III} , yielding untapered NWs with constant diameter and exponential length increase over time; (ii) *Simultaneous axial-radial growth regime*, which begins when the NW length exceeds λ_{III} and radial growth starts, with more complex NW morphologies emerging depending on growth conditions and NW material. The radial growth dynamics thus depends strongly on the growth parameters. In particular, the growth temperature increases λ_{III} , the V/III ratio influences the sidewall nucleation probability, and the group III precursor ratio influences the adatom mobility and λ_{III} . Also the material system and crystal phase influence the process, due to the different surface energetics and possible polarity of the facets influencing adatom binding. These last aspects will be discussed more in detail in the following section on the crystal phase of the NWs.

2.1.2 Crystal phase and crystal defects in III-V NWs

III-V semiconductor NWs typically crystallize either in the cubic ZB or in the hexagonal WZ phase. The ZB structure, also known as *sphalerite*, is the stable bulk crystal phase for most III-V compounds, with the exception of nitrides. It consists of two interpenetrating face-centred cubic lattices of group III and V atoms, each atom tetrahedrally bonded to four neighbours of the opposite type (Figure 2.1.2 (a)). The main distinction between ZB and WZ lies in their stacking sequence along the close-packed

$\langle 111 \rangle$ or $\langle 0001 \rangle$ directions: ABCABC for ZB in the $\langle 111 \rangle$ direction and ABAB for WZ in the $\langle 0001 \rangle$ direction. Each letter corresponds to one of the three possible positions of the III-V atomic bilayers, as shown in Figure 2.1.2 (b). During the NW growth, deviations from these ideal sequences often occur, leading to crystal defects. The most common planar defect in NWs is the *stacking fault* (SF), which arises when one or more atomic layers nucleate in the wrong sequence (Figure 2.1.2 (c)). For instance, in a NW growing along the $[0001]$ direction, the expected sequence is WZ-like (ABAB). If a layer nucleates in position C, the stacking becomes ABABABCACACA, with the “ABC” part being compatible with the ZB sequence. Another frequent defect is the *twin plane*, where the stacking sequence mirrors across a “twin” layer (Figure 2.1.2 (d)). Starting from the ZB sequence ABCABC, for example, the defected stacking $ABC\bar{A}CBACB$ corresponds to a twin boundary across the $\bar{A}$ plane. In addition to stacking faults and twins, polytypism can also occur in NWs, with higher-order polytypes such as 4H or 6H^{79,80}. This thesis focuses on InP and $\text{InAs}_x\text{P}_{1-x}$ NWs grown along the $\langle 100 \rangle$ and $\langle 0001 \rangle$ directions. Although the discussion will emphasize this material system, the general concepts are valid for III-V NWs in general. While certain applications may benefit from defect engineering^{81,82}, most optoelectronic and electronic devices require defect-free NWs. This is because ZB and WZ phases exhibit distinct bandgaps: WZ-InP and WZ-InAs, for example, are characterized by larger bandgaps compared to their ZB counterparts^{83–85}. This bandgap

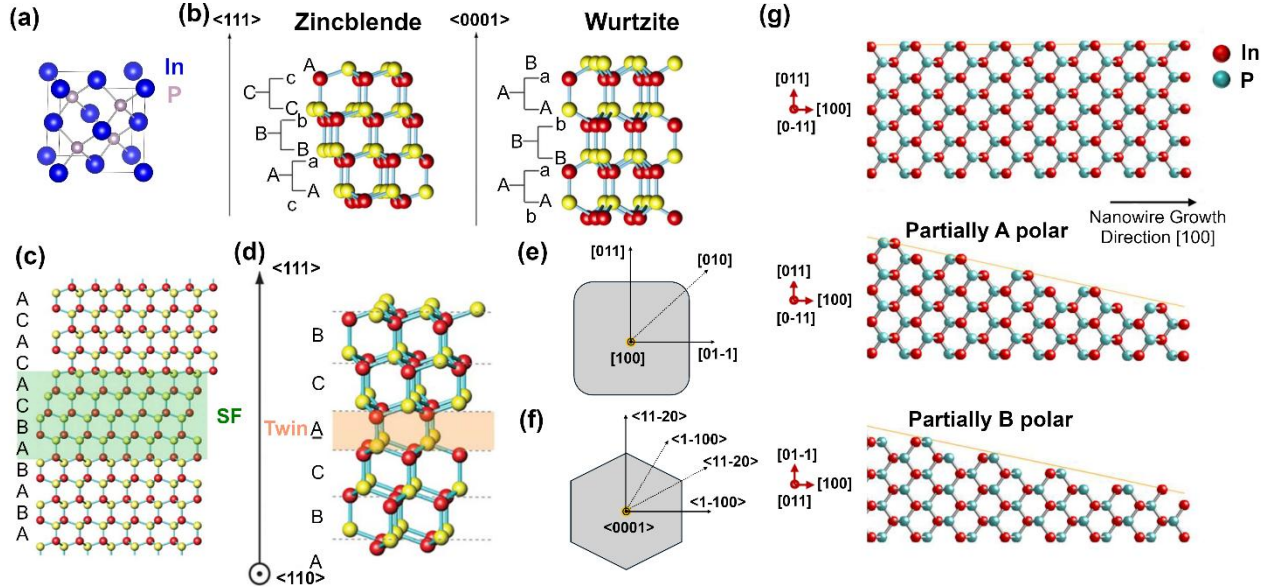


Figure 2.1.2: (a) InP zincblende unit cell ; (b) Stacking sequence of ZB and WZ crystal phases, adopted from Ref. 85 ; (c) ZB stacking fault inside a mainly WZ stacking sequence, adopted from Ref. 85 ; (d) Twin plane inside a ZB stacking sequence, adopted from Ref. 85 ; (e) Typical facets observed in ZB InP NWs grown along the $\langle 100 \rangle$ direction; (f) Typical facets of InP NWs grown along the $\langle 0001 \rangle$ direction with a WZ crystal phase; (g) ZB InP NWs facets polarity dependence. Adopted from Ref. 68.

difference has been experimentally demonstrated^{86–89} and also exploited for the realization of crystal phase QDs⁸⁶, where abrupt ZB/WZ transitions act as confinement potentials. However, uncontrolled inclusions of ZB segments within a mainly WZ NW result in charge traps, degrading optical properties. Likewise, SFs and twin boundaries can scatter carriers^{90,91} and phonons⁹², limiting charge transport and thermal conductivity. Achieving defect-free NWs remains a major challenge, particularly for pure WZ phases, which are unique to the NW geometry and rarely stable in bulk III-V semiconductors. InP is especially challenging: growth along $\langle 0001 \rangle$ yields the lowest stacking fault energy among III-Vs^{93,94}, making SFs very likely. Conversely, growth along $\langle 100 \rangle$ favours ZB and is typically stacking-fault free. Overall, NW crystal phase purity (whether ZB or WZ) is governed by several key parameters:

- *Material system.* The competition between covalent sp^3 bonding and electrostatic interactions determines phase stability. Thus, materials with stronger ionicity, such as nitrides, tend to crystallize in WZ, while phosphides and arsenides are more prone to defects and polytypism⁹⁵.
- *Growth substrate orientation.* Certain orientations stabilize one phase over the other. For example, $\langle 100 \rangle$ generally promotes ZB, as rotational twins cannot form parallel to the growth front of the NW, while $\langle 0001 \rangle$ growth often results in WZ with frequent SFs.
- *NW diameter.* Reduced catalyst size favours WZ, since surface energy contributions dominate the energetic of the NW at small diameters. In particular, pure WZ InP NWs have only been demonstrated for catalyst diameters below 20 nm^{96–99}, whereas InAs can maintain WZ up to 56 nm¹⁰⁰. It must be mentioned that radial overgrowth preserves the crystal phase of the NW core, allowing thicker defect-free WZ NWs to be obtained by growing shells on thin pure WZ cores¹⁰¹.
- *Growth conditions.* Parameters such as growth temperature, V/III ratio, and growth technique strongly affect NW crystal phase. For InP and InAs, higher temperatures generally favour WZ^{102,103}, while lower temperatures stabilize ZB. Temperature acts in a non-trivial way on the growth of NWs since it influences the energetics of the growth, the adatoms diffusion and possible crystal reconstructions. A high V/III ratio has been reported to stabilize WZ^{104,105}, though the underlying mechanisms remain under debate.

Finally, the crystal phase and growth direction also determine the sidewall facets of the NWs - i.e. the flat low-energy crystal planes that constitutes the NW sidewalls - which strongly influence surface energetics and growth dynamics. ZB [111] NWs typically expose $\{110\}$ or $\{112\}$ facets, while WZ NWs show $\{1-100\}$ or $\{11-20\}$ facets (Figure 2.1.2 (f)). In contrast, $\langle 100 \rangle$ -oriented NWs with ZB crystal phase often exhibit $\{110\}$ or $\{100\}$ facets (Figure 2.1.2 (e)). Some of these facets can show polarity or partial polarity, in case the facets show only one type of atom or both elements but in unequal numbers, respectively. For example, concerning ZB InP NWs grown along the $\langle 100 \rangle$ direction, it was discussed by Fonseka et. al.^{68,106} that (011) and (0-1-1) facets grow faster than the (01-1) and (0-11) side facets due to the different polarity. In fact, although if $\{011\}$ planes should be in principle non-polar, the presence of a tapering angle typical of the NW, make the first couple of facets rich in In (A-polar) and the second one P-rich (B-polar) (Figure 2.1.2 (g)). The facet polarity is interesting since it affects the type of atoms and dangling bonds, inducing differences in reactivity, surface energies and growth rates, deeply affecting the growth dynamics of the NW^{107,108}.

2.1.3 NWs axial heterostructures: achievements and challenges

It has already been discussed that the ability of NWs to accommodate large strain is a key advantage, as it enables the realization of highly lattice-mismatched heterostructures. Such heterostructures can be engineered both axially and radially by tuning the NW growth mode, and can involve either group III or group V material changes. In this brief overview, I will focus on the axial heterostructures that are mainly explored in this thesis. While the heterostructure of highly lattice mismatched materials like InAs-InP represents a major advantage of NWs, two critical challenges often arise in practice: (i) difficulties in maintaining straight NW growth and (ii) the formation of abrupt, atomically sharp interfaces. Straight growth is not always achieved, as heterostructures frequently exhibit kinking or even downward growth (i.e., a change of the growth direction to a different crystallographic orientation or to the opposite direction, respectively). The preferential NW growth direction is usually the one that minimizes the NW surface free energy¹⁰⁹, which is strongly influenced by several factors including growth temperature, precursor fluxes, heterostructure composition, interruptions during growth, the orientation/faceting

of the NW and its crystal phase. Two main mechanisms are generally considered responsible for kinking of the NW. The first is the instability of the triple phase line at the catalyst-NW-vapor interface, a dynamic process well described in Refs. 110, 111. The second involves the displacement of the metal catalyst droplet itself¹¹². The dominant mechanism depends on the material system and the growth direction, making precise control of kinking non-trivial. Focusing on InAs/InP heterostructures, it is well established that the growth of one interface (InAs on InP) is less challenging than the reverse (InP on InAs)¹¹³. This asymmetry is explained by differences in interface energetics: the system tends to minimize the interfacial energy between dissimilar materials. Nevertheless, under optimized growth conditions, both interfaces can be successfully realized. Most demonstrations of axial InAs/InP heterostructures have been obtained in WZ NWs grown along the $\langle 0001 \rangle$ direction. Here, a key parameter is the In concentration within the catalyst NP, which determines the droplet contact angle and influences its possible displacement¹¹³. Much less is known about the same heterostructure in ZB NWs grown along $\langle 100 \rangle$, although these structures have shown extreme sensitivity to the In content in the catalyst, with controlled kinking experimentally demonstrated in pure InP NWs. To date, however, no systematic studies exist for InP/InAs heterostructures in the $\langle 100 \rangle$ direction, which are provided in this thesis for the growth of the NW-QDs.

The second major challenge is achieving abrupt interfaces. This is particularly difficult in heterostructures involving group III material interchange, due to the so-called *reservoir effect*^{52,114}: the group III element is retained within the catalyst alloy for some time after switching precursors, leading to a graded composition across the interface. Growth interruptions are often employed to sharpen such interfaces, by pausing group III incorporation and allowing a delay before introducing the new material. However, such interruptions can also enhance the probability of kinking. Despite these challenges, group V material interchange is less tricky and sharp InAs/InP interfaces have been successfully achieved in the $\langle 0001 \rangle$ direction by exploiting the dependence on In concentration in the catalyst¹¹⁵.

2.2 Quantum Dots for Telecom Emission: state of the art.

Semiconductor QDs are widely regarded as promising building blocks for future quantum communication technologies, as they represent an exceptionally versatile platform for realizing both quantum light sources and spin-photon interfaces which are key elements for the development of quantum repeaters. Unlike conventional single-photon sources, such as spontaneous parametric down-conversion or attenuated laser pulses which suffer from severe trade-offs between brightness and single-photon purity, QDs are predicted to deterministically generate on demand single photons, and even entangled photon pairs, with high efficiency. QDs are nanostructures in which charge carriers are confined in all three spatial dimensions, resulting in a delta-like density of states and discrete energy levels similar to those of atoms, earning the name of *artificial atoms*. In particular, solid state semiconductor QDs offer engineering of their energy levels through control of their size, shape, and composition. Experimentally, these QDs are realized by embedding a low-bandgap material with dimensions smaller than the exciton Bohr radius^{116,117} within a higher-bandgap host matrix. Quantum confinement in the small QD dimension leads to the formation of excitonic complexes due to strong Coulomb interactions of the carriers, which are responsible for the characteristic optical emission of the QDs. The emission, in fact, arises from the radiative recombination of excitonic states, producing single photons with well-defined energies in a deterministic manner. Moreover, by exploiting magnetic fields or coupling between two QDs, it is possible to engineer a discrete Λ -type energy structure – an essential feature for generating multiphoton entangled cluster states that are a crucial component of efficient quantum repeaters^{2,4} and quantum memories^{2,6,118}. Nevertheless, coupling between the solid state QD and its environment can limit photon purity and indistinguishability, which are important factor defining a single photon emitter. *Single photon purity* is a quantification of the multi-photon emission probability relative to single-photon emission and is measured with the second-order autocorrelation function at zero delay $g^{(2)}(0)$, which must be lower than 0.5 to have single photon emission. *Indistinguishability* is the degree to which two photons emitted by the source are identical in frequency, polarization, and spatial mode. A major drawback of solid state semiconductor QDs relies in the interactions of confined excitons with phonons or with charge traps in the surrounding matrix, generating fluctuating electric fields on the QD that induce dephasing and spectral diffusion.

Experimentally, semiconductor QDs are realized with Stranski-Krastanov (SK-QDs) growth or Droplet Epitaxy (DE-QDs). SK-QDs are probably the most known and developed epitaxial QD technique due to its fabrication simplicity, which exploit the strain-driven growth at the interface between two highly lattice-mismatched materials. To release the strain, by properly tuning the growth conditions, an island-growth mode is developed, which lead to the quantum confinement of carriers in the island. SK-QDs have typically a density dependent from the lattice-mismatched of the employed materials and with difficulties in its control, a shape that can be tuned by the growth conditions but typically suffers of asymmetries. Conversely, DE-QDs have been proposed as a good alternative to account for the SK-challenges. DE-QDs relies in the deposition of group III droplets at controlled conditions which can crystallized into islands- i.e. QDs – by the following group V deposition, leading to the possibility of decouple the QD density and dimension and leading to symmetric QDs. Epitaxially grown semiconductor QDs have already demonstrated outstanding performances as single-photon and entangled-photon sources. For instance, state-of-the-art InGaAs QDs have achieved generation of photonic cluster states with entanglement lengths up to ten photons and emission rates of 0.5 GHz¹¹⁹. However, these performances have been primarily achieved in the near-infrared (NIR) range, around 900-960 nm of wavelength¹²⁰. For practical quantum communication applications, especially those involving long-distance with transmission channels up to 500 Km⁵ which relies on optical fibers, operation in the *telecom wavelength* range is essential. The telecom bands are a wavelength range typically employed in telecommunication field, and it is divided in five bands: (i) “original” O-band (1260 nm – 1360 nm); (ii) “extended” E-band (1360 nm – 1460 nm); (iii) “short” S-band (1460 nm – 1530 nm); (iv) “conventional” C-band (1530 nm – 1565 nm), and (v) “long” L-band (1565 nm – 1625 nm). In particular, optical fibers exhibit minimum transmission losses of 0.35 dB/km at 1310 nm (O-band) and 0.2 dB/km at 1550 nm (C-band), making these wavelength windows optimal for quantum communication and a long-term goal for the research in the field of photons emitters. In addition, these bands correspond to regions of low solar background noise and minimal Rayleigh scattering, and they benefit from a mature technology already developed for classical optical communication, including high-performance laser wide-band optical modulators, and superconducting NW single-photon detectors. Achieving efficient QD emitters operating in the telecom O- and C-bands remains a major technological challenge. The most promising material systems are

InGaAs/GaAs and InAs/InP. InGaAs/GaAs QDs, typically emitting below 920 nm at cryogenic temperatures, require strain-engineering strategies to redshift the emission to telecom wavelengths. This can be achieved through various approaches in SK-QDs, such as the use of low-In-content $\text{In}_x\text{Ga}_{1-x}\text{As}$ strain-reducing layers¹²¹, metamorphic buffer layers¹²², or vertically coupled double QD layers¹²³. In contrast, the InAs/InP material system is naturally suited for telecom emission due to its band-alignment. However, the mismatch of 3.2% poses challenges for SK-QDs growth, leading to excessively high QD densities ($>10^{10} \text{ cm}^{-2}$) and large QD sizes, resulting in emission often beyond 1600 nm. Additional complications, such as As/P intermixing, further affect emission control. These issues can be mitigated by using ultrathin InGaAs or InAlGaAs interlayers or double-capping techniques. Overall, although the promising performance of SK-QDs, the challenge of scalability is clear due to a poor control of the QD density and directionality of the emission¹²⁴.

In this framework, embedding QDs in III-V semiconductor NWs emerges as a highly promising platform. NW-QDs combine several advantages:

- *Dislocation-free heterostructures*: the radial strain relaxation in NWs allows integration of lattice-mismatched materials without dislocations formation, eliminating the need for strain engineering.
- *Density and position control (scalability)*: due to the VLS approach, an high degree of control of the QD density and position is possible using lithographically defined catalysts or low density of colloids. This makes NW-QDs a scalable platform.
- *Tunable morphology and composition*: QD dimensions can be finely tuned – lateral size by catalyst diameter and thickness by growth time – while maintaining compositional and density control.
- *Crystal phase engineering*: both ZB and WZ phases can be obtained by adjusting growth conditions and orientations.
- *In situ waveguide integration*: NW geometry inherently allows the formation of an optical waveguide around the QD, enhancing light extraction efficiency without post-growth processing. Cone-shaped NWs with smooth tapering can act

as nanoantennas¹²⁵, realizing a waveguiding effect and adiabatically funnelling emitted photons along the axial direction.

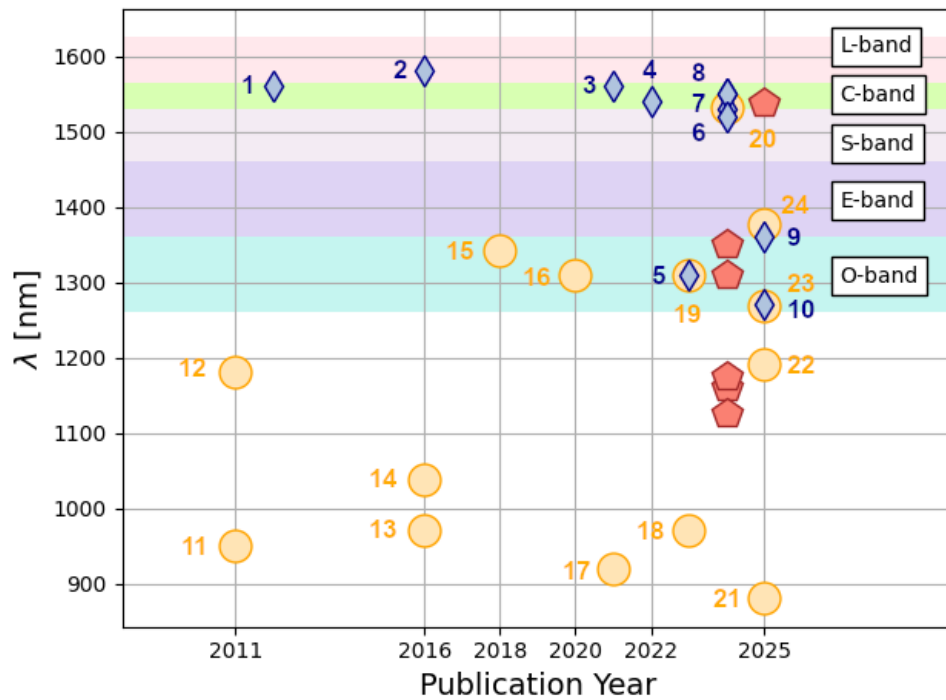
- *Axial stacking*: multiple QDs can be axially stacked within a single NW, enabling coupled or entangled QD systems and Λ -like energy structures for cluster-state generation.

The InAsP/InP system has attracted particular attention for NW-QDs platform. Most studies have focused on small diameter (~ 18 - 20 nm) WZ-phase NWs grown along the $\langle 0001 \rangle$ direction, demonstrating single-photon emission around 950 nm^{97,126} with high purity ($g^2(0) = 0.002$)¹²⁷. The WZ phase along the $\langle 0001 \rangle$ direction is particularly interesting for some applications due to the predicted nearly vanishing fine structure splitting (FSS), allowing emission from the exciton-biexciton cascade that produce polarization-entangled photon pairs¹²⁸. However, challenges remain: $\langle 0001 \rangle$ -oriented WZ InP NWs are prone to stacking faults and crystal defects that limit QD lateral dimensions and complicate emission tuning toward the C-band. Additionally, WZ material parameters are less well characterized than their ZB counterparts, complicating theoretical modelling. Efforts to push NW-QDs emission into the telecom range have been done by controlling the As-content inside the $\text{InAs}_x\text{P}_{1-x}$ QD and by increasing the QD dimensions. Due to the typical growth scheme employed for these QDs, the increase and control of As content in the QD results challenging for the high amount of As required for the telecom emission¹²⁷. Thus, the only way to redshift the emission in such mandatory small diameter QDs (which avoid the presence of SF in the WZ InP matrix), is to increase the QD thickness bringing the aspect ratio toward high values $t_{\text{QD}}/D_{\text{QD}} = 0.4$. High QD aspect ratio is expected to bring the heavy and light hole ground states together, allowing mixing an polarization change of the ground state which results in a experimentally observed dramatic drop of the brightness due to a less efficient coupling into the HE_{11} mode of the NW¹²⁷. The realization of optimized waveguides to increase the signal from these emitters at telecom bands have been achieved employing a combined SAE-VLS approach^{127,129}, which improve the brightness of one order of magnitude at the telecom O-band. However, the signal level achieved in the telecom is still not sufficient. Recent advances include the realization of dot-in-a-rod structures, consisting of a high-As $\text{InAs}_x\text{P}_{1-x}$ QD embedded within a lower-As $\text{InAs}_y\text{P}_{1-y}$ rod, all within an InP NW. This design allows telecom emission due to higher As incorporation in the QD while

maintaining favourable QD aspect ratios (~ 0.26) and higher brightness at telecom O-¹³ and C-band¹⁵. Excitation below the InP bandgap further reduces charge noise and linewidth broadening. Nevertheless, a decrease in brightness with increasing emission wavelength remains a challenge which is observed, likely due to the larger aspect ratios and possibly blinking effects. Figure 2.2 reports some points of QDs emission wavelength achieved vs. the publication year. The blue rhombus are from SK- and DE-QDs, while the orange circles are the reports in literature from NW-QDs. It is possible to observe that, for the NW-QDs, achieving the Telecom O- and C-band required a great effort compared to the SK for the reason explained above. In red, for comparison, the results obtained during this PhD project are given. The number in the graphic are correlated with the corresponding reference, which is provided in the Appendix A2.

In summary, while significant progress has been achieved, the realization of NW-QDs in the telecom range still requires further optimization – particularly regarding QD geometry avoiding high QD aspect-ratio, defect control, and light-extraction efficiency.

Figure 2.2: State of the art of the emission wavelength obtained from QDs published for SK and DE growth mode (blue rhombus) and for NW-QDs (orange circles). In red, the points achieved and published in this thesis are reported for comparison.



Chapter 3: Experimental methods

Introduction

In this chapter, a brief overview about the experimental methods employed during this project will be presented. The substrate preparation, the NW growth technique and their structural, morphological, and optical characterization techniques are discussed. All the semiconductor NW samples employed in this work have been grown by means of chemical beam epitaxy (CBE) (Section 3.2), with the typical substrate preparation explained in Section 3.1. For the morphological study, a scanning electron microscope (SEM) has been employed, while a transmission electron microscope (TEM) is used for the structural study of the crystals (Section 3.3). The chemical analysis of the alloys is conducted through Energy-dispersive X-ray spectroscopy (EDS) (Section 3.4), employing TEM or SEM depending on the crystal dimensions. In particular, EDS-TEM has been employed for the catalyst composition, while EDS-SEM to determine the NW composition. The optical characterization is conducted employing micro-photoluminescence (μ -PL) measurements (Section 3.5). All these techniques will be presented in the following.

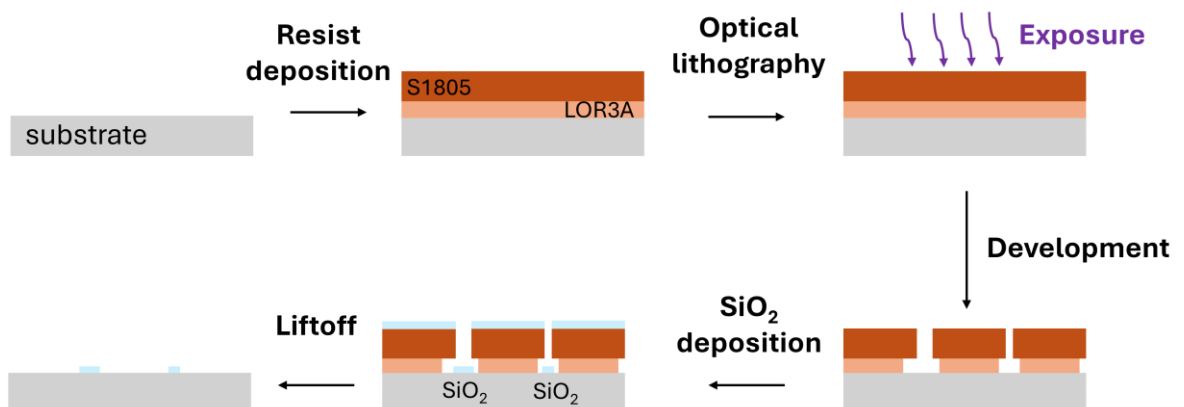
3.1 Substrate preparation

In this thesis, Au catalyzed VLS growth of the NWs is employed as the main technique for the NW growth. This approach requires the deposition of gold catalyst particles onto the growth substrate. The Au particles are deposited using a commercial water solution

of gold colloids (BBInternational EM.GCnn) with different nominal diameters, in particular (10 ± 1) nm, (20 ± 1) nm, and (30 ± 2) nm are used throughout this thesis. Colloids are deposited on a dummy Fe-doped InP(100) or InP(111)B substrate. Prior to deposition, the substrates are cleaned in a 50°C acetone (ACE) bath to remove dust and organic residues, rinsed in isopropanole (IPA) and blow-dried with nitrogen (N_2). To promote colloids adhesion, the substrate surface is functionalized with poly-L-lysine, which is drop-casted on the substrate surface for 30s, rinsed in de-ionized water (DI-water) and blow-dried with N_2 . Colloidal solution is diluted in water in dependence by the desired density and drop casted for few seconds on the substrate surface, which are then rinsed in DI-water and blow dried with N_2 .

Prior to the colloid deposition, for the samples used for the optical characterization, SiO_2 markers are realized on the substrate employing standard optical lithography. These markers allows a precise localization of individual NWs at the micrometer scale during the μ -PL measurements. Figure 3.1 provides a schematic of the fabrication process for these markers. Initially, the sample is cleaned in ACE and IPA and baked at 170°C for 5 minutes, to remove the moisture and promote a good adhesion of the photoresist mask. A layer of LOR3A is spin-coated at 4000 rpm for 1 minute and soft-baked at 170°C for 3 minutes. A second photoresist layer of S1805 is spin-coated at 5000 rpm for 1 minute and baked at 115°C for 1 minute. The marker pattern is then defined on the resist by means of optical lithography, employing a Durham Magneto Optics MicroWriter ML3 system which ensures a resolution of about 0.6-1 μ m. The exposure dose is of 90 mJ/cm². The sample is then developed in MF319 for 75 seconds and deep rinsed in DI-water for 30 seconds to stop the development process. A descum step using oxygen plasma is performed for 75 seconds at 30 W, to remove resist residuals. A 20 nm thick SiO_2 layer

Figure 3.1: Schematic of the SiO_2 marker fabrication with optical lithography and SiO_2 deposition.



is deposited by means of a radio frequency (RF) magnetron sputtering, employing a RF power of 150 W and an Argon flow of 26 sccm, resulting in a deposition rate of 1.8 Å/s. Liftoff is carried out overnight in ACE, followed by rinsing in IPA. Finally, a second liftoff step is performed in MF319 for 10 minutes to remove the LOR3A layer.

3.2 Chemical Beam Epitaxy

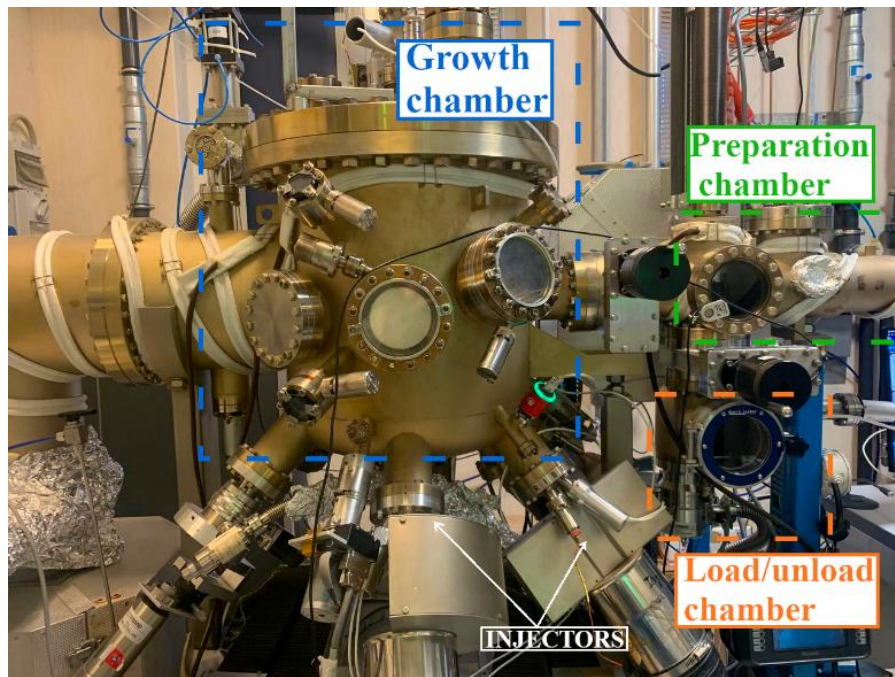


Figure 3.2: Ribier-Compact 21 CBE system employed for the growth of the samples at NEST laboratories in Pisa. The three chambers are highlighted, as well as the injectors , which provide the precursor fluxes for the growth.

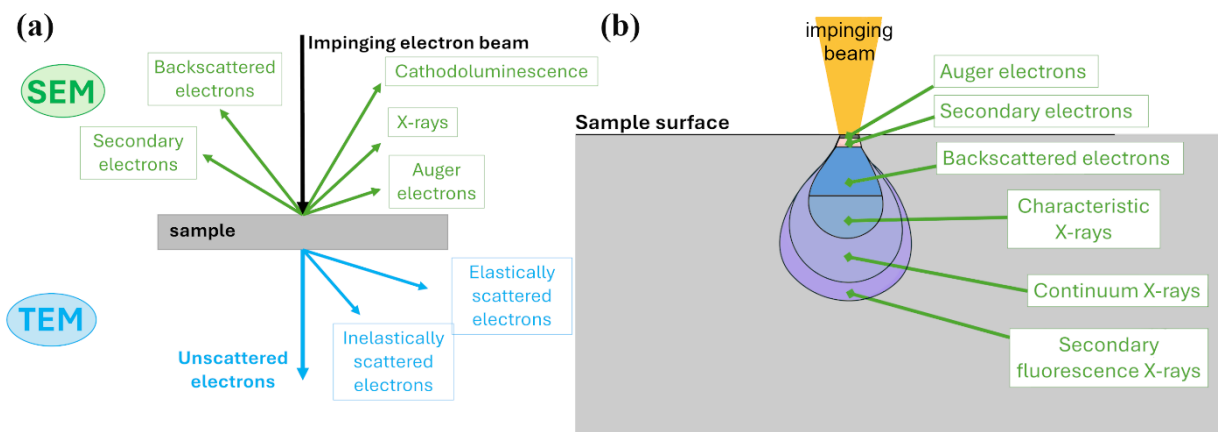
The main objective of this thesis is the realization of NW-QD structures with a fine control over composition, size, and crystal structure. Therefore, a bottom-up epitaxial growth technique is required. Epitaxial growth is typically performed employing techniques such as CBE, molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD). In this thesis, a Ribier-Compact 21 CBE system is employed and presented in Figure 3.2. CBE is an ultra-high vacuum (UHV) technique that enables epitaxial growth with atomic-layer precision^{130,131}. It combines the advantage of a UHV chamber typical of MBE, which allows high purity of the grown samples and a ballistic flux for the growth, with the flexibility of gaseous metalorganic (MO) compounds typical of MOCVD. The system is composed by three main chambers connected by gate valves:

a load-lock, a preparation chamber, and a growth chamber. The *load-lock chamber* is pumped by a turbo molecular pump, which maintains a base pressure of $\sim 10^{-8}$ Torr. It is used for the introduction of the growth substrates in the CBE system without compromising the vacuum in the other chambers. The *preparation chamber*, typically held at $\sim 10^{-10}$ Torr base pressure by an ion pump, is used for the substrate storage and outgassing. In fact, prior to the growth, the substrates are outgassed at 300°C on a heating stage to remove moisture and other contaminants before the transfer to the growth chamber. The *growth chamber* is a stainless steel chamber surrounded by cryopanelled cooled with liquid nitrogen, which help decreasing the growth chamber base pressure by surface trapping of contaminants and residual gases on the wall via cryopumping. A combination of turbomolecular and a ion pumps allows the chamber to reach a base pressure of $\sim 10^{-9}$ Torr, and a working pressure during growth in the range of $\sim 10^{-6}$ - 10^{-5} Torr, depending on the precursor fluxes. The growth chamber is equipped with an electron gun and a fluorescent screen for in situ Reflection High-Energy Electron Diffraction (RHEED) to study surface reconstruction during the growth and check for the average crystal purity of the grown samples. The growth substrate is typically indium-bonded on a molybdenum plate, mounted upside-down on a rotating manipulator. The substrate temperature is controlled through a thermocouple kept on the back of the plate and measured employing an optical pyrometer, with an accuracy of $\pm 10^\circ\text{C}$. The CBE system is equipped with several group III and V gaseous MO precursors. *Trimethylindium* (TMIn), *triethylgallium* (TEGa), and *tris(dimethylamino)antimony* (TDMASb) are MO precursors delivered directly to the substrate surface and thermally decomposed there. In contrast, *tertiarybutylarsine* (TBAs) and *tertiarybutylphosphine* (TBP) are pre-cracked at 1000°C in high-temperature injectors, supplying for arsenides and phosphides reactive AsH_3 and PH_3 species for the growth¹³². The fluxes of the precursors are controlled adjusting their line pressures using a DSP9000 baratron which gives the feedback for the opening or closing of a needle valve in the line. The line pressure is proportional to the actual flux on the substrate in the growth chamber. The precursors are introduced in the chamber for the growth by a RUN valve, which allows the gas to flow through the injectors. When the MO precursor is not in use, a VENT valve directs them to an exhaust line and a dry scrubber. This configuration allows also to stabilize the fluxes in the VENT mode before switching to RUN mode for the growth. Furthermore, each injector is also equipped with a shutter to enable a rapid cut-off of the precursor flux during the growth.

3.3 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

Electron-matter interactions have been a fundamental tool for the morphological and structural characterization in the field of nanoscience. The ability to overcome the diffraction limited regime, typical of conventional optical methods (limited to $\sim\lambda/2$), has enabled spatial resolution down to the nanometer and even atomic scale. When an electron beam interacts with a sample, various signals result from this interaction. These signals can be collected either in transmission or in reflection mode, as schematically illustrated in Figure 3.3 (a) in green and blue, respectively. Reflection-based detection is employed in scanning electron microscopy (SEM) technique. In SEM, the most commonly detected signals are the *Secondary Electrons*, with energies lower than 50 eV and which provide topographical information, and *Backscattered Electrons*, high-energy electrons sensitive to the atomic number (Z-contrast) and which provide compositional information. In addition, *X-rays* emitted from the sample can be used for chemical composition analysis with Energy dispersive X-ray spectroscopy (EDS) (see Section 3.4). In SEM imaging, the electron beam scans the sample in a raster pattern, and the interaction between the electron beam and the thick sample results in a *interaction volume*

Figure 3.3: (a) Schematic of types of interactions between an electron beam and a thin sample, both in scattering and transmission mode; (b) Schematic of the interaction volume responsible for the type of signal detected in SEM.



from which the different signals are generated, as schematized in Figure 3.3(b). In this thesis, two different SEM systems are used to morphologically characterize the NWs and for composition analysis. In particular, a SEM Zeiss Merlin equipped with a GEMINI II column has been employed for the morphological characterization. The SEM is used operating at 5 keV and 100 pA beam current. Images were acquired in top view to assess the NW density and cross sections shape, and at 45° tilt to observe the overall NW morphology. For EDS analysis, a Zeiss Ultraplus field emission SEM equipped with a GEMINI II column and with a Bruker Quantax EDS detector is used to characterize the ternary alloy segments within the NWs.

For higher-resolution structural and chemical analysis, including the quantum dot characterization and the catalyst composition, a JEOL JEM-F200 Multipurpose Transmission Electron Microscope (TEM) was employed¹³³, allowing both conventional TEM and Scanning TEM (STEM) imaging. This system operates at 200 kV and it is equipped with a Schottky field-emission gun and a silicon-drift EDS detector. For TEM, the interaction of the electron beam with the sample is detected in transmission mode. In this case, the beam passes through a thin sample and it can be scattered elastically or inelastically. When the electron beam is parallel, the sample is measured in TEM mode; if it is convergent and scanned across the sample point-by-point in a raster pattern, the STEM mode is employed. In TEM mode, the image is detected in bright field by a Gatan RIO16 CMOS camera, enabling high-resolution imaging. A selected area electron diffraction (SAED) can provide crystallographic information through diffraction analysis. In STEM mode, an High Angle Annular Dark Field detector (HAADF) collects scattered electrons to form Z-contrast images, with a spatial resolution down to 0.16 nm. This mode also allows for precise localization of compositional features via EDS analysis. In this thesis, TEM mode is employed to check the crystal structure of the NWs and to identify the presence of defects such as stacking faults and twin planes, while STEM mode is typically employed to analyse the QD morphology and dimension within the NWs. The atomically-resolved STEM measurements presented in Chapter 4 (Figure 4.3.2 (d) and (e)) are obtained employing a Spectra 200-COLDFEG (by Thermo Fisher) equipped with condense lens-aberration corrected, a dual EDS detector with 1.7 Sr effective solid angle, with the possibility to achieve a STEM resolution of 60 pm at 200 kV. These

measurements are done in collaboration with Prof. Beatriz Galiana Blanco from University of Carlos III de Madrid (Spain).

3.4 Energy-Dispersive X-ray spectroscopy

In this thesis, the chemical composition analysis of the NWs is investigated using Energy-Dispersive X-ray spectroscopy (EDS), performed in both SEM and TEM configurations. EDS is an analytical technique based on the detection of characteristic X-ray emission derived from the interaction of materials with an high energy electron beam (see Figures 3.3). When the energetic electron beam impinges on the sample, it can ionize atoms ejecting inner-shell electrons. As result, electrons from higher-energy shells fall into the lower-energy vacancies, releasing the energy difference in the form of an X-ray. This emitted X-rays are characteristic of the element from which they originate, providing a fingerprint for elemental identification. Typical X-ray signals detected from the electron beam-sample interaction are *continuous X-rays* (or *Bremsstrahlung X-rays*), *characteristic X-rays* and *secondary fluorescence X-rays*. Continuum X-rays arise from the deceleration of the primary impinging electron beam, creating a background in the spectrum which is typically subtracted during the quantitative analysis. Secondary fluorescence X-rays occur when the X-rays emitted by one atom excite neighbouring atoms, causing additional X-ray emission. This phenomenon can artificially increase the intensity of certain peaks, leading to overestimation of specific elements and lowering the spatial resolution of the measurement. Finally, the characteristic X-rays are the fingerprints of the elements present in the sample and are directly used for the qualitative and quantitative EDS analysis. By evaluating the intensity of the characteristic X-ray peaks, the concentration of the relative atom can be evaluated. In particular, for SEM-EDS the quantitative analysis includes *ZAF correction*, which improves the accuracy of elemental quantification by taking into account three effects on the characteristic X-ray: the atomic number (Z) effect, the absorption effect (A), and the fluorescence excitation effect (F). In TEM-EDS, due to the thinness of the sample, the absorption and the fluorescence effect can be disregarded and the so-called “*Cliff-Lorimer Ratio*” method is employed for quantitative analysis.

3.5 Optical characterization

The optical characterization of the samples in this thesis have been done through *micro-photoluminescence* (μ -PL) measurements, performed at both room temperature and at cryogenic temperature (10K). PL is a well-established, non-destructive spectroscopic technique used to investigate the electronic and optical properties of nanostructures and, more in general, materials. It exploits an electromagnetic field as a probe to excite the system, creating an electron-hole couple. When the system relaxes to the ground state, the electron-hole recombines emitting a photon which can be detected (PL signal) and has an energy dependent by the electronic structure of the system. It is possible to excite the sample with different excitation schemes. The *non-resonant excitation* consists in the excitation of the system with an energy higher than the emitted photon energy, typically with values above the semiconductor bandgaps (for a bulk material) or of the bandgap of the matrix material in which QDs are embedded. For QDs, subsequently to the optical excitation, carriers are first relaxed to the lowest excited states non-radiatively and then to the ground state by radiative recombination, emitting a photon whose energy depends by the quantum confinement, the Coulomb interaction energy and the bandgap of the material. Other excitation schemes are the *resonant* or *quasi-resonant excitation*. Here, the exciting energy is equal or almost equal to the optical transition under study and it can be employed to benefit for the less complex spectra, since typically less excitonic complexes are excited, and a reduced background emission. However, these excitation schemes are more technically demanding, since they requires to filter the excitation signal from the PL signal and the cross section of the individual emitters is reduced. Excitation can also be implemented *in continuous wave (CW)* or *pulsed mode*. In the former, the energy is constantly supplied to the investigated structure, leading to a constant time-averaged occupation of each state. However, this can also introduce sample heating. In contrast, the pulsed mode provides a higher instantaneous power for a short period of time, enabling to create an high number of carriers and the possibility to observe the evolution of their distribution, a technique called *time-resolved PL*. PL have a spatial resolution typical of hundreds of μm to mm size and is particularly suitable for bulk materials. When the structures under investigation are nanostructures, like QDs, the

necessity of an excitation area of μm /sub- μm dimensions is mandatory. This is typically achieved by focusing the excitation signal on the nanostructure employing an optical or confocal microscope and, typically, a piezoelectric stage to control the movements. In this case, $\mu\text{-PL}$ is performed instead of PL.

A schematic of the $\mu\text{-PL}$ setup employed in this thesis is presented in Figure 3.5. A semiconductor continuous-wave laser diode with $\lambda = 640\text{ nm}$ is used to excite the NW-QDs non-resonantly above the energy bandgap of InP. It passes through a neutral density (ND) filter to control the excitation power and a power meter is used to monitor it. The beam is then focused onto the sample through a long working distance (20 mm) infinity-corrected microscope objective, with a numerical aperture (NA) of either 0.4 or 0.6. This configuration produces a laser beam spot size of approximately $2\text{ }\mu\text{m}$ in diameter, requiring a density at maximum of $\sim (5 \times 10^7)\text{ QDs/cm}^2$, to measure single nanostructures. The $\mu\text{-PL}$ signal emitted by the NW-QDs is collected by the objective and directed into a 1-meter focal length monochromator. The dispersed signal is detected by a nitrogen-cooled multichannel InGaAs linear array photodetector, which enables efficient detection in the telecom wavelength range. To minimize thermal effects, the sample is mounted on a cold finger of a liquid helium continuous-flow optical cryostat, which maintains the system at low temperature of 10K during the measurements. The $\mu\text{-PL}$ measurements are performed at the Wrocław University of Science and Technology (Poland), in collaboration with the group of Prof. Grzegorz Sęk. The $\mu\text{-PL}$ measurements for the Appendix A1 are performed at University of Rome La Sapienza (Italy) in collaboration with the group of Prof. Marta De Luca, with a similar setup.

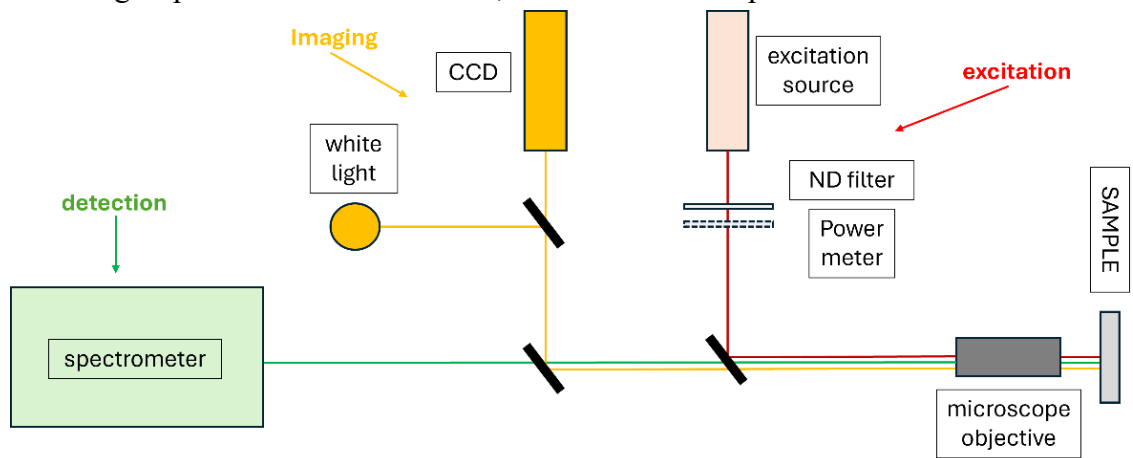


Figure 3.5: $\mu\text{-PL}$ set up, where the three main optical path for the excitation, the imaging and the QDs emission are highlighted in red, yellow and green, respectively.

Chapter 4: Growth and optical characterization of zincblende $\text{InAs}_x\text{P}_{1-x}$ QDs in InP NWs

Introduction

NW-QDs capable of emitting single photons in the telecom band have already been investigated in the literature^{14,134}, as discussed in Chapter 2. The use of NWs as a platform for such emitters offers several advantages compared to other types of QDs, such as SK-QDs or DE-QDs. Among the possible material combinations explored for telecom emission, $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP NWs have attracted much attention. Commonly, these NW-QDs are grown with a WZ crystal phase along the $\langle 0001 \rangle$ growth direction in thin NWs (diameters up to ~ 20 nm), with a low As fraction in the alloy material ($x \sim 0.25$) and exhibiting single-photon ground-state emission at ~ 950 nm^{97,98,127,129,135–138}. Recently, emission in the telecom O- and C-bands has been achieved by varying the QD thickness and increasing the As fraction in the alloy^{127,139}. However, increasing the As content in the QD is challenging with the growth protocol employed in literature, furthermore due to the constraint in WZ NWs of very small diameters of 20 nm, increasing the thickness of the QD results in high QD aspect ratio ($t_{\text{QD}}/D_{\text{QD}}$), leading to a dramatic decrease in the brightness toward the telecom bands^{13,127}. Furthermore, phenomena such as kinking¹⁴⁰ and downward growth¹⁴¹ have been reported for alternating InP and InAs segments in Au-assisted grown NWs. Alternative growth strategies have been proposed, including more complex heterostructures such as the “dot-in-a-rod” design¹³, in which a high-As-content QD ($x \sim 0.68$) is first embedded in a segment of $\text{InAs}_x\text{P}_{1-x}$ with lower As fraction ($x \sim 0.5$) and then embedded in an InP NW. InAs/InP axial heterostructures have also been investigated along the $\langle 0001 \rangle$ direction with a pure WZ crystal phase, mainly in InAs NWs^{142–144}. Despite the good results achieved for WZ NWs grown along the $\langle 0001 \rangle$ direction, this orientation is prone to easy

stacking faults formation, which represents a great disadvantage. In fact, crystal phase purity is a crucial parameter for QD emission, as stacking faults are highly detrimental to the optical quality of the emitter. In particular, stacking faults can act as charge traps that confine carriers along the NW axis while allowing free motion perpendicularly to it, thereby creating a varying electrostatic environment around the QD. This results in significant emission-line broadening via so-called spectral diffusion^{97,98}, as well as reduced photon coherence time and indistinguishability. InP NWs grown along the $\langle 0001 \rangle$ direction have shown a pure WZ crystal phase only for very thin catalyst diameters (≤ 20 nm) and by properly choosing the growth conditions^{96,100,145}. Along this growth direction, the ease of stacking-fault formation is due to the small energy difference between the WZ and zincblende (ZB) stacking sequences, with an energy barrier for the WZ/ZB transition of ~ 3.4 meV/atom in InP NWs with diameters larger than 20 nm¹⁴⁶. Conversely, NWs grown along the $\langle 100 \rangle$ direction show a pure ZB crystal phase over a wide range of diameters and growth conditions¹⁴⁷, since the only stable stacking sequence in the $\langle 100 \rangle$ direction is the ZB^{148–150}. The strict requirement of ultrathin catalyst diameters in the WZ InP NWs limits the tunability of the QD lateral dimension, making the achievement of emission in the telecom band more difficult and complicating the manipulation and fabrication of such NWs. Therefore, a thorough investigation of WZ crystal phase control in larger diameter NWs is important (see Chapter 6). Alternatively, the issue can be addressed by choosing a different approach by changing the growth direction of the system from $\langle 0001 \rangle$ to $\langle 100 \rangle$, thereby obtaining pure ZB InP NWs. These are typically obtained by growing on InP(100) substrates where, depending on annealing pre-growth conditions and growth conditions, NWs can be oriented along the $\langle 100 \rangle$, $\langle 111 \rangle$ or $\langle 110 \rangle$ direction^{68,106}. However, to the best of my knowledge, only pure InP NWs have been investigated along the $\langle 100 \rangle$ direction, without growing InAs/InP heterostructures.

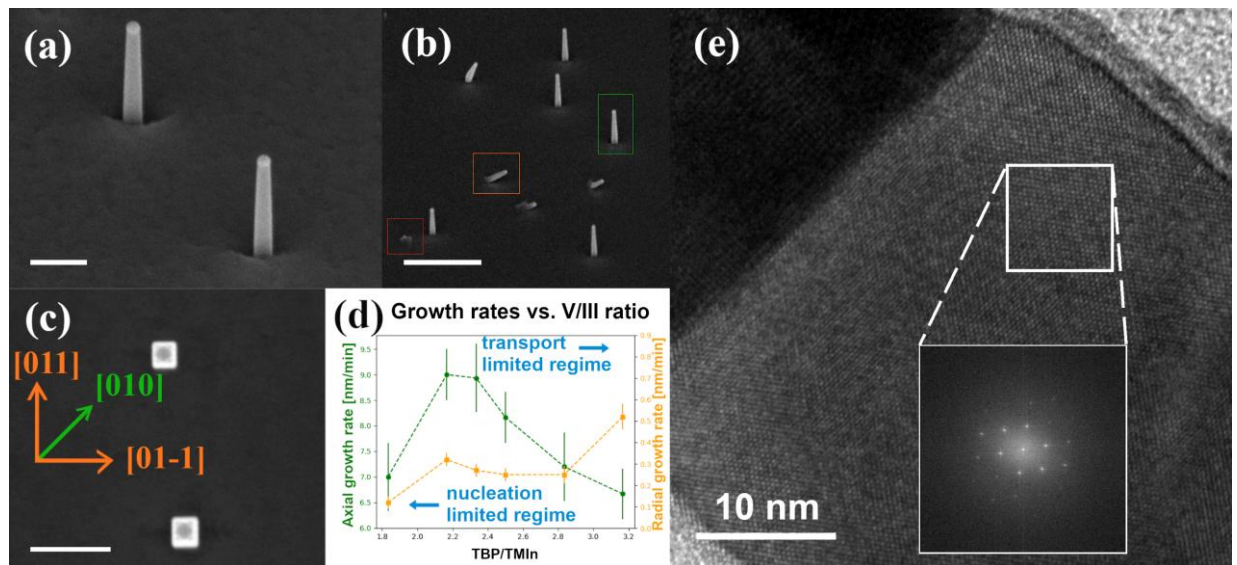
In this chapter, the growth of InP NWs along the $\langle 100 \rangle$ direction is first discussed in Section 4.1, comparing the grown samples with the literature studies. Section 4.2 explores the growth of InAs_xP_{1-x} segments on top of InP NWs, highlighting the associated growth challenges. Section 4.3 focuses on the growth of QDs and the final NW-QD structure obtained. Finally, Section 4.4 demonstrates the tunability of emission with QD

composition and dimension, and Section 4.5 summarizes these chapter findings. The results presented in this chapter are published in Ref.16.

4.1 Zincblende InP nanowires growth

InP NWs grown along the $\langle 100 \rangle$ direction were obtained using as a catalyst 30 nm gold colloids dispersed on an InP(100) substrate. Figures 4.1(a-c) show a representative sample grown at $(390 \pm 5)^\circ\text{C}$ with TMIn and TBP line pressures of 0.30 Torr and 0.60 Torr, respectively. Panels (a) and (b) present 45° -tilted side-view SEM images at different magnifications, revealing a NW morphology which is almost untapered. In particular, panel (b) highlights the same three different NW morphologies previously reported by *Fonseka et. al.*¹⁰⁶. In our sample, 72% of the NWs are oriented along the desired $\langle 100 \rangle$ direction (green box in the image), 11% are kinked into the $\langle 111 \rangle$ direction (orange box), and 17% are grown planar to the substrate surface (red box). Percentages were estimated from a count of 100 NWs. Panel (c) shows a top-view SEM image of the NW square base cross section, with nearly symmetrical $\{011\}$ facets.

Figure 4.1: (a) Example of a 45° -tilted side-view SEM image of InP NWs grown along the $\langle 100 \rangle$ direction with a ZB crystal phase employing TMIn and TBP line pressures of 0.30 Torr and 0.60 Torr, respectively (scale bar: 200 nm); A lower magnification image is presented in panel (b), with the three type of oriented NWs discussed in the main text (scale bar: 1 μm); (c) top-view SEM images of InP NWs with a square cross-section made of $\{011\}$ -type facets (scale bar: 200 nm); (d) Axial (green) and radial (orange) growth rates as a function of the V/III ratio; (e) Bright field HR-TEM image of an InP NW, showing a pure ZB crystal phase. This is confirmed by the image FFT in the inset.



To determine the optimal growth conditions for InP NWs, different samples were grown at $(390 \pm 5)^\circ\text{C}$ with varying V/III ratios, by changing the TBP line pressure while keeping the TMIn line pressure fixed at 0.30 Torr. In Figure 4.1 (d), the dependence of the axial (green) and radial (orange) growth rates on the V/III ratio is plotted, clearly individuating distinct growth regimes. At low V/III ratios, the growth is limited by the nucleation of solid phase, with the availability of group V adatoms controlling the growth rate. Increasing the group V supply increases the axial growth rate of the NWs⁶¹. At higher V/III ratios, the system enters in a transport-limited regime, where the excess of group V adatoms hinders the diffusion of group III adatoms to the growth interface, effectively slowing down the axial growth rate^{103,151}. Moreover, high TBP line pressures enhance the vapor-solid growth mechanism, as evidenced by the increased radial growth rate at the highest ratio, which competes with the VLS mechanism and leads to greater NW tapering. The optimal untapered NW morphology with high enough axial growth rate is obtained with TMIn and TBP line pressures of 0.30 Torr and 0.60 Torr, respectively. Figure 4.1 (e) shows a bright field HR-TEM image of the tip of a representative NW grown under these conditions, revealing a pure ZB crystal phase, as confirmed by the FFT in the inset. No stacking faults are detected along the entire NW axis in any of the examined NWs.

4.2 Growth of InP/InAsP heterostructures in nanowires.

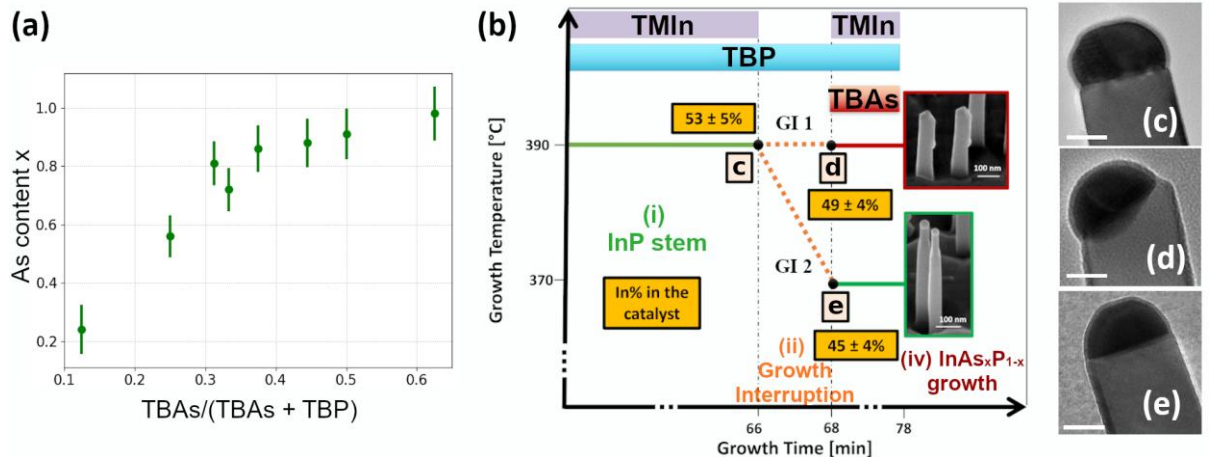
After selecting the optimal growth conditions for the initial InP segment (hereafter referred to as the “*stem*”), the growth of ternary $\text{InAs}_x\text{P}_{1-x}$ segments on top of the InP stem is discussed in this section. The aim is to grow the entire $\text{InAs}_x\text{P}_{1-x}$ range of composition, with particular interest on high As fraction “ x ”. $\text{InAs}_x\text{P}_{1-x}$, in fact, spans with the composition the direct tunable band gap range of 0.351 eV - 1.351 eV¹⁵². Due to the band alignment with InP, higher As content enables emission in the telecom bands, which is highly desirable, but also potentially increases the growth challenges and it can lead to easier kinking of the NWs. The protocol used to grow different $\text{InAs}_x\text{P}_{1-x}$ segments on top of InP stems comprises the following steps:

- (i) Growth of the InP stem using the optimized conditions discussed in Section 4.1.

- (ii) Performing a *growth interruption* (GI) after the InP stem growth by stopping the TMIn supply inside the chamber while maintaining TBP supply. This GI is necessary to adjust and stabilise the TBP and TBAs line pressures for the desired ternary composition of the following QD/InAs_xP_{1-x} segment growth. It can lead to an improvement of the heterostructure interfacial sharpness^{153–156} and a better control of the As content in the QD, by a proper adjustment of the fluxes.
- (iii) Resume growth by reintroducing TMIn in the chamber, together with TBAs and TBP to form the InAs_xP_{1-x} segment.

We have investigated the growth of InAs_xP_{1-x} with compositions ranging from $x = 0.24 \pm 0.08$ to 0.90 ± 0.08 . Figure 4.2.1 (a) reports the calibration curve of the alloy. The As incorporation (x-index) is plotted in function of the partial pressure of TBAs. For all compositions tested, the GI strongly affected the resulting heterostructure. Figure 4.2.1 (b) schematises two GI protocols, denoted “GI 1” and “GI 2”. GI 1 consists of interrupting the supply of TMIn, preparing TBAs and TBP line pressures for the desired InAs_xP_{1-x} segment composition while keeping the sample at the InP stem temperature (390 °C). This protocol results in a downward-growth mode, as shown in the red inset of panel (b) for an InAs_{0.88}P_{0.12} segment grown after the InP stem. GI 2, on the other hand, differs only in that the sample temperature is lowered by 20 °C during the GI. This procedure yields

Figure 4.2.1 (a) InAs_xP_{1-x} calibration curve of the incorporation of As vs. TBAs partial pressure; (b) Schematic representation of the growth protocols investigated for the growth of InP stem with InAsP segments, highlighting the two different growth interruptions “GI 1” and “GI 2”; (c) HRTEM image of the catalyst droplet at the top of the InP stem immediately before the GIs; (d) HRTEM image of the catalyst droplet at the InP NW top right after the GI 1, showing the nanoparticle destabilization; (e) HRTEM image of the catalyst droplet at the InP NW top right after the GI 2, evidencing a stable catalyst following the GI 2 procedure.



straight heterostructures (green inset in Fig. 4.2.1 (b)). The different behaviour can be ascribed to a destabilization of the catalyst nanoparticle. To elucidate the GI effect on the nanoparticle, three different samples have been grown:

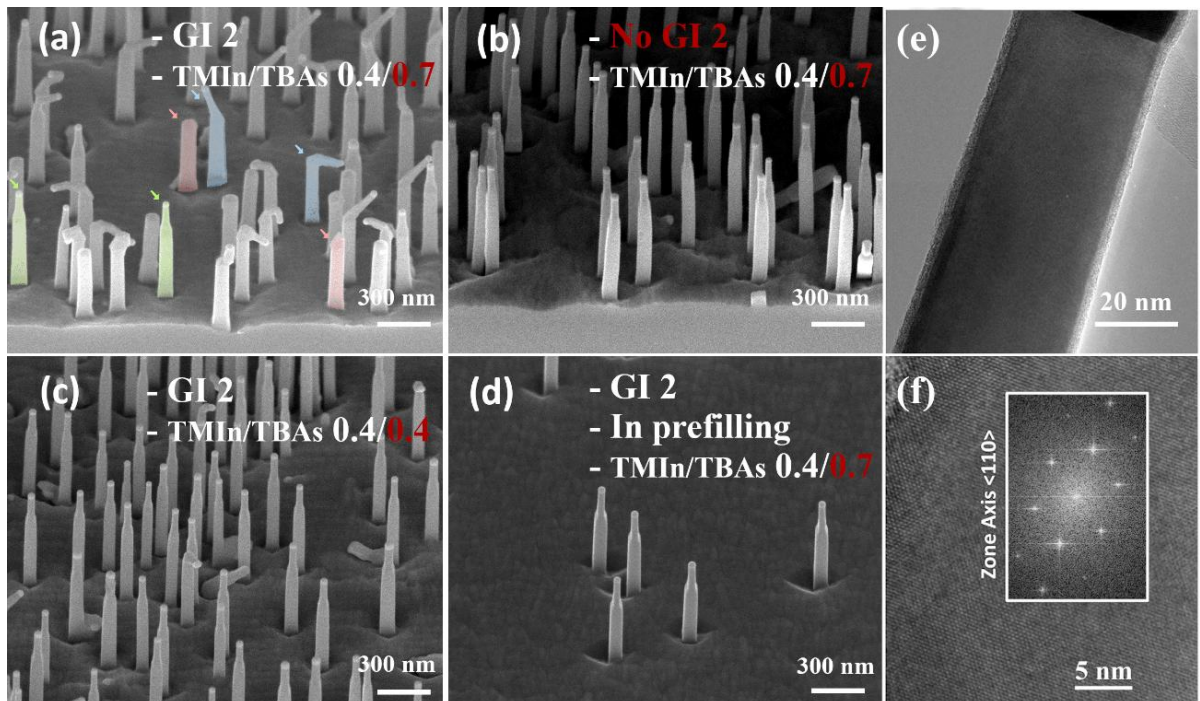
1. A InP stem, stopping the growth of the NW before the GI;
2. A sample with GI 1, but stopped before the $\text{InAs}_x\text{P}_{1-x}$ growth.
3. A sample with GI 2, but stopped before the $\text{InAs}_x\text{P}_{1-x}$ growth.

All these samples were cooled down under identical conditions with no group-V flux in the UHV chamber. This cooldown procedure has been shown not to significantly alter the catalyst composition during the growth¹¹³. For both GI protocols, a decrease of the In content in the catalyst from $(53 \pm 5)\%$ to lower values is observed. However, not a significant difference is found between GI 1 and GI 2, measuring a In content of $(49 \pm 4)\%$ and $(45 \pm 4)\%$, respectively. The small difference between GI 1 and GI 2 indicates that the absolute change in catalyst of the In content alone does not account for the distinct growth modes observed. HRTEM measurements, however, reveals a clear difference in catalyst stability immediately after GI 1 and before the $\text{InAs}_x\text{P}_{1-x}$ growth. Panels (c), (d), and (e) of Figure 4.2.1 show TEM images of the catalyst droplet before the GI, right after GI 1 and right after GI 2, respectively. After GI 1, 98% of the analysed NWs (out of 50 NWs in total) display a non-straight interface between the NW and the catalyst, leading to sliding of the nanoparticle down the sidewalls once the $\text{InAs}_x\text{P}_{1-x}$ growth starts. In contrast, after GI 2, 100% of the analysed NWs exhibit a flat interface, resulting in a straight InP/ $\text{InAs}_x\text{P}_{1-x}$ heterostructure for all the ternary alloy composition investigated. A similar temperature-dependent stability of the catalyst already been reported in the literature for InP NWs grown along the $\langle 0001 \rangle$ direction¹⁵⁷, where unpinning of the catalyst nanoparticle from the NW top and its sliding down the NW sidewall occurs when TMIn feeding is interrupted at high growth temperature. This unpinning process has been attributed to a reduction in catalyst supersaturation caused by high temperature and low P flux during the growth interruption. In fact, such a condition favors the formation of a truncated area at the NW top, allowing the catalyst droplet to wet the NW sidewalls and, when the growth is resumed, the catalyst promote epitaxial growth of solid phase along the NW sidewall in a downward direction. From these observations, we conclude that achieving a straight NW heterostructure requires maintaining a flat interface between the

catalyst and the InP stem after performing the GI, with the critical parameter being the temperature at which the GI is performed. An additional requirement to have a straight morphology is however observed when a pure InAs segment is grown on top of the InP stem. Figure 4.2.2 (a) shows a 45°-tilted SEM view of a sample where an InAs segment is grown on top of the InP stem after GI 2, employing TMIn and TBAs line pressures of 0.40 Torr and 0.70 Torr, respectively. In this case, three different growth modes are observed – straight, kinked, and downward - highlighted in green, blue and red, respectively. In this case, the conditions required for the growth of straight $\text{InAs}_x\text{P}_{1-x}$ are therefore insufficient for pure InAs, likely due to an instability occurring in the first layers of InAs growth. Straight growth of pure InAs can be obtained with three different strategies:

- (i) Avoiding the GI. In fact, for pure InAs, TBAs can be stabilized without being introduced in the growth chamber during the last minutes of the InP stem

Figure 4.2.2 SEM side-view images of InP NW stems followed by InAs segment growth under different conditions: (a) by employing GI 2 followed by InAs growth with TMIn and TBAs line pressures of 0.40 Torr and 0.70 Torr, respectively. NWs exhibiting downward, kinked and straight morphologies are highlighted in red, blue and green, respectively; (b) no GI and employing TMIn and TBAs at 0.40 Torr and 0.70 Torr respectively; (c) with GI 2, followed by InAs grown employing TMIn and TBAs line pressures both at 0.40 Torr; (d) with GI2 followed by In catalyst prefilling and TMIn and TBAs at 0.40 and 0.70 Torr, respectively; (e) representative TEM image of an InAsP segment, as well as an HRTEM image in panel (f) demonstrating the absence of crystal defects; in the inset, an FFT of the image performed in the $\langle 110 \rangle$ zone axis demonstrate that the phase of this segment is pure ZB.



growth and without affecting its growth. For this reason, it is possible to completely avoid the growth interruption and directly grow InAs at the same stem temperature by employing TMIn and TBAs at 0.40 Torr and 0.70 Torr, respectively, at the same temperature of the InP stem. This strategy results in straight NWs, as shown in the SEM image of Figure 4.2.2 (b).

- (ii) Performing GI 2 but reducing the TBAs flux. In panel (c) of Figure 4.2.2 a sample grown employing TMIn and TBAs line pressure of 0.40 Torr and 0.40 Torr are reported, showing a straight morphology.
- (iii) Performing GI 2 followed by In prefilling and growing InAs maintaining the same line pressure of TMIn and TBAs of 0.40 Torr and 0.70 Torr, respectively. In panel (d), a sample grown performing a 30 s In prefilling after GI 2 at 0.3 Torr is reported, showing also in this case a straight morphology.

All three strategies share the feature of increasing the In content in the catalyst prior to InAs growth. In fact, avoiding the GI (strategy (i)) preserves the higher In content present at the end of the InP stem growth, as already shown for the $\text{InAs}_x\text{P}_{1-x}$ growth. Decreasing the TBAs line pressure for InAs growth (strategy (ii)) decreases the V/III ratio, which is linked to a higher In content in the catalyst for the InAs growth¹⁵⁸. Lastly, employing a In prefilling directly supplies In in the Au droplet. We therefore believe that, while for $\text{InAs}_x\text{P}_{1-x}$ the main critical parameter is the temperature at which the mandatory GI is performed, for pure InAs a sufficiently high In content in the catalyst is additionally required. This latter behavior has already been observed in InAs NWs grown on GaAs stems along the $\langle 0001 \rangle$ direction¹⁴² and during the switch from InP to InAs along the $\langle 0001 \rangle$ direction¹⁴³. Likely, pure InAs growth requires a higher droplet contact angle to satisfy the well known Neelson-Shchekin stability condition:

$$\frac{\gamma_{WV}}{\gamma_{LV}} < \sin\beta - \cos\beta \quad (3.3.1)$$

with γ_{WV} being the solid-vapor surface energy, γ_{LV} the liquid-vapor surface energy and β the droplet contact angle¹⁴². This In supply in the catalyst is probably not necessary for $\text{InAs}_x\text{P}_{1-x}$ due to differences in surface energies compared to pure InAs, affecting in a different way the nanoparticle stability condition. Finally, Figure 4.2.2 (e) shows a TEM image of an $\text{InAs}_x\text{P}_{1-x}$ segment without any crystal defect, while panel (f) presents an

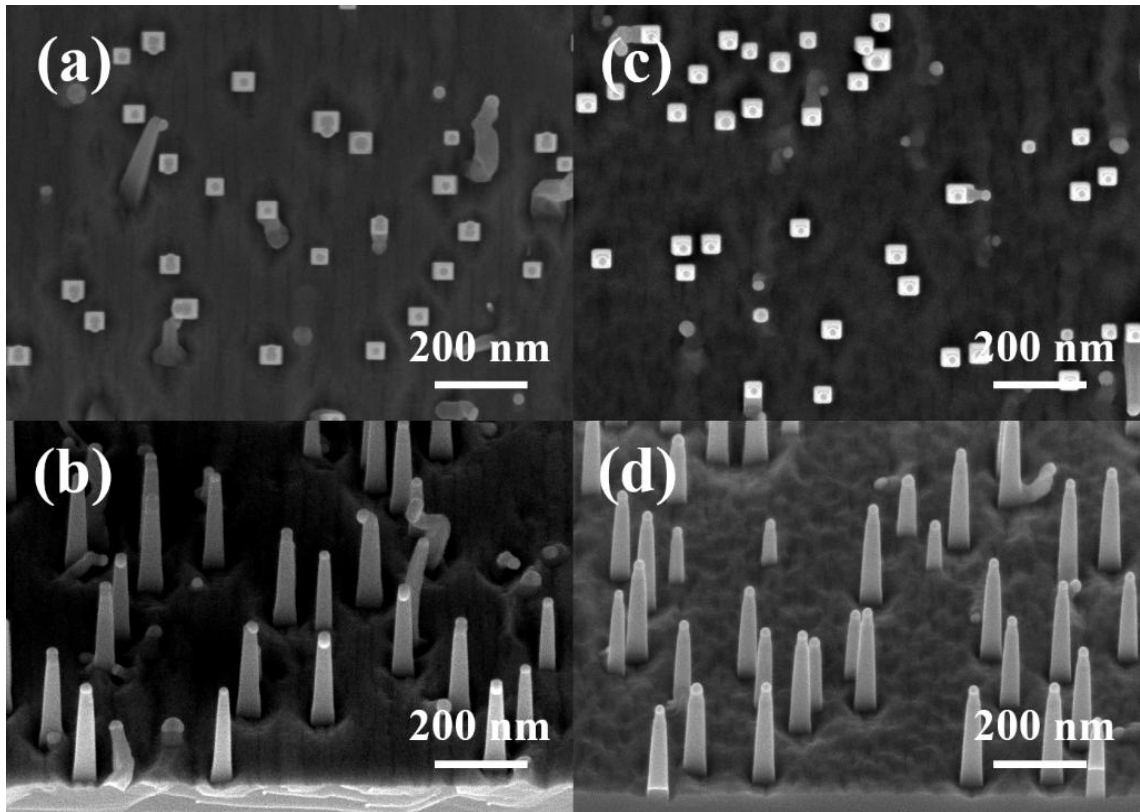


Figure 4.3.1 (a) top view and 45°-tilted view (b) SEM images of a $\text{InAs}_{0.88}\text{P}_{0.12}$ NW-QDs sample grown with TMI and TBP line pressures after the QD of 0.30 Torr and 0.60 Torr, respectively. The NWs kink after the QD growth at the InAsP/InP interface. When the InP tip growth is conducted right after the QD employing TMI and TBP 0.30 Torr and 1.00 Torr, respectively, almost all NWs are straight, like it is shown in panel (c) top view and panel (d) 45°-tilted side view SEM images.

HRTEM image and its FFT, confirming the pure ZB crystal phase also of the $\text{InAs}_x\text{P}_{1-x}$ segment.

4.3 Zincblende $\text{InAs}_x\text{P}_{1-x}$ QD growth for telecom emission.

In the previous sections, it is discussed how it is possible to grow an $\text{InP/InAs}_x\text{P}_{1-x}$ heterostructure along the $\langle 100 \rangle$ direction in a pure ZB crystal phase, covering the full composition range from $x = 0.25$ to $x = 1.00$ (i.e., pure InAs). Now, we focus on the final NW-QD structure. To grow the QD, the growth strategies describe in the previous sections are applied, but with a shorter $\text{InAs}_x\text{P}_{1-x}$ growth time, followed by the growth of an InP segment tip on top of the $\text{InAs}_x\text{P}_{1-x}$ using TMI and TBP line pressures of 0.30 Torr and 1.00 Torr, respectively. For the upper interface of the QD, it is observed to be necessary to grow the InP tip under a higher group-V flux compared to the stem. Figure

4.3.1 shows two samples grown with different TMIn and TBP fluxes for the InP tip after the QD. In particular, panels (a) and (b) display top-view and a 45°-tilted side-view SEM images of a sample where the InP tip is grown employing TMIn and TBP line pressures for the InP tip equal to the ones of the stem (0.30 Torr and 0.60 Torr, respectively). In this case, 45% of the NWs, out of a total of 50 NWs counted, are kinked at the $\text{InAs}_x\text{P}_{1-x}/\text{InP}$ interface after the QD. Increasing the TBP line pressure to 1.00 Torr resulted in straight InP tips in all the NWs of the ensemble, as shown in panels (c) and (d). This behaviour is consistent with previous reports on InP NWs grown along the $\langle 100 \rangle$ direction, where a low In fraction inside the catalyst was associated with a switching in the growth direction from $\langle 100 \rangle$ to $\langle 111 \rangle$ ¹⁵⁹, and with observations in InAs/InP heterostructures grown along the $\langle 0001 \rangle$ ^{113,160}. Figure 4.3.2 (a) shows a 45°-tilted SEM image of a representative NW-QD ensemble, containing a 10 nm thick $\text{InAs}_{0.88}\text{P}_{0.12}$ QD. The final samples are grown by employing the optimize growth strategy discussed in Section 4.2, growing for 5 min an InP tip after the QD employing TMIn and TBP line pressures of 0.30 Torr and 1.00 Torr, respectively, and by switching back the line pressures to those of the stem (i.e. TMIn and TBP line pressure of 0.30 Torr and 0.60 Torr) for 1 hour, to passivate the QD with an InP shell. Indeed, it is possible to observe that during the axial growth of the InP tip after the QD, also a significant InP radial growth at the NW sidewalls takes place, resulting in tapered NWs. This InP radial growth is beneficial, as it provides a passivation layer and it can be eventually exploited for the epitaxial growth of a waveguide, as it will be discussed in Chapter 5. Due to the square cross section of the ZB NWs, the QD shape is typically a truncated pyramid, with a major base side length of $L_{\text{base}} \sim 55$ nm and a minor top side length of $L_{\text{top}} \sim 45$ nm. A schematic of the NW and QD shape is reported in Figure 4.3.2 (b). To study the tunability of the emission and its dependence on the QD features, QDs with different compositions and thicknesses are grown. We focused particularly on high-x $\text{InAs}_x\text{P}_{1-x}$ QDs, as telecom-band emission is expected for high As content in the QD. Figures 4.3.2 (c) present a STEM image of a representative QD with a thickness of 10 nm and $x = 0.80$, with the QD position being highlighted by a blue arrow. Interestingly, it is also possible to observe the presence of a $\text{InAs}_x\text{P}_{1-x}$ shell, highlighted with orange lines. In panel (d), an TEM-EDS map is reported, where it is possible to observe the presence of As (in yellow) along this shell. The $\text{InAs}_x\text{P}_{1-x}$ shell originates from a parasitic radial growth on the NW sidewalls during the QD growth. From the HR-TEM image of panel (e), the $\text{InAs}_x\text{P}_{1-x}$ shell thickness is

consistent with 2-3 monolayers. This parasitic radial growth has never been reported for QDs grown in the $\langle 0001 \rangle$ direction in the WZ crystal phase^{97,98,127,129,135,136,138,161}, except in Ref.144, where it was localized near the QD and does not extend all over the NW stem length. Conversely, it is observed in ZB NWs¹⁶² and is likely related to the favourable radial growth on the $\{011\}/\{010\}$ facets due to their surface energies. While the InP shell is beneficial for the QD passivation, this parasitic $\text{InAs}_x\text{P}_{1-x}$ shell may be detrimental to the QD emission in terms of both line broadening and reduced intensity. In fact, the carrier wave functions confined in the QD can partly leak out into the shell, making them more sensitive to the surface states and acting as non-radiative recombination centers and

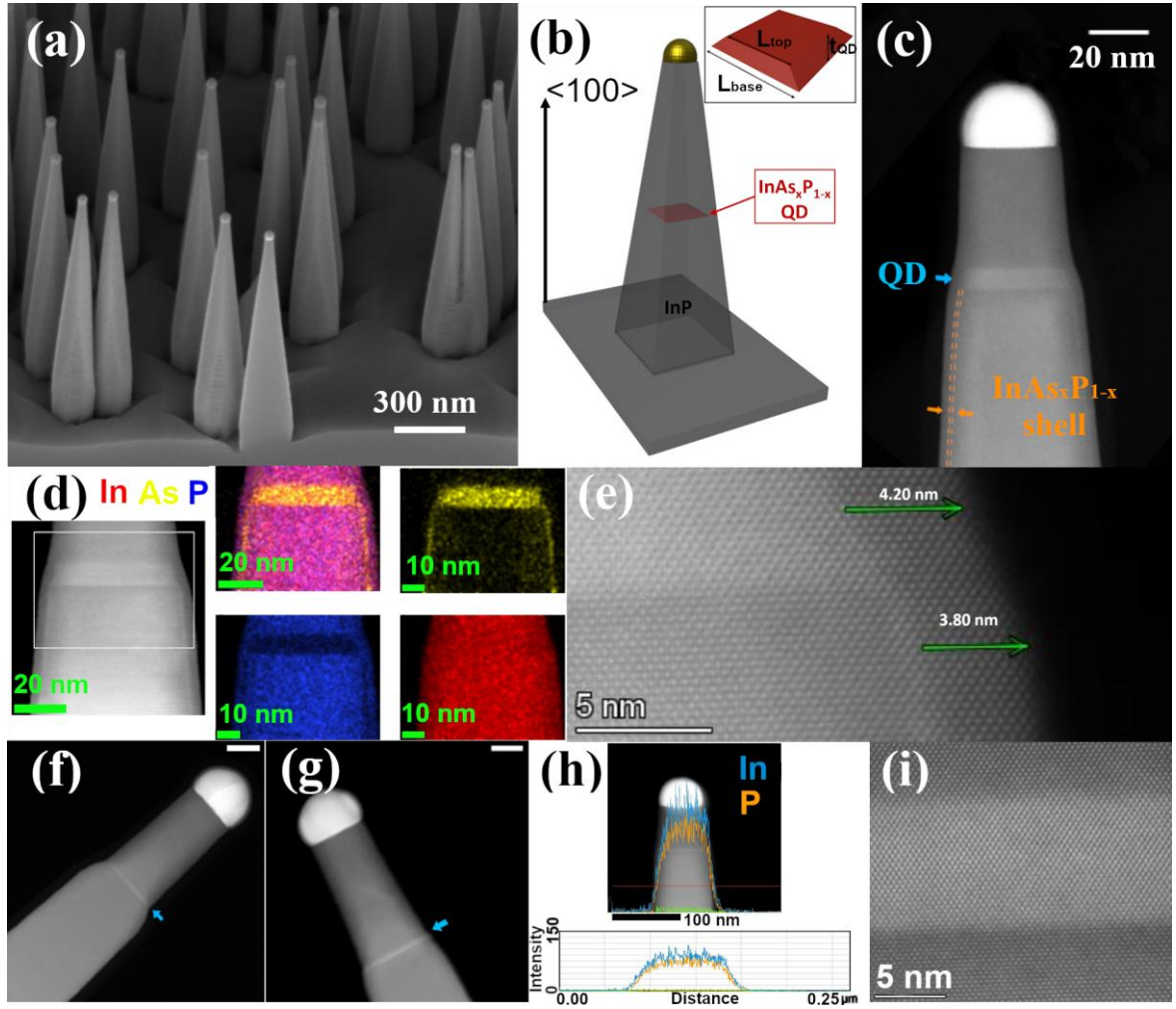


Figure 4.3.2 (a) 45°-tilted SEM image of a representative final NW-QD sample, here consisting of a 10-nm thick $\text{InAs}_{0.80}\text{P}_{0.20}$ QD embedded within InP NWs ; (b) Schematic representation of the QD geometry, with the $\text{InAs}_x\text{P}_{1-x}$ QD (in red) embedded in a InP NW (in grey). In the inset, the truncated pyramid shape of the QD is shown; (c) STEM image of a 10 nm $\text{InAs}_{0.80}\text{P}_{0.20}$ QD (highlighted with a blue arrow) and the presence of the $\text{InAs}_x\text{P}_{1-x}$ parasitic shell grown at the NW sidewalls, highlighted in orange; (d) TEM-EDS maps performed on the same QD of panel “e”, where the presence of the $\text{InAs}_x\text{P}_{1-x}$ shell is particularly clear; (e) HR-TEM image of the $\text{InAs}_x\text{P}_{1-x}$ shell; (f) STEM image of a 3 nm thick $\text{InAs}_{0.88}\text{P}_{0.12}$ QD (scale bar: 20 nm); (g) STEM image of a 3 nm thick InAs QD (scale bar: 20 nm); (h) TEM-EDS line scan analysis on a 3 nm thick $\text{InAs}_{0.88}\text{P}_{0.12}$ QD at the red line height, showing the absence of As detection in the NW; (i) HR-TEM image of a $\text{InAs}_{0.80}\text{P}_{0.20}$ QD, demonstrating crystal purity at the QD height.

carrier loss channels. Thus, the QD excitons can be more exposed to fluctuations of the charges on the NW sidewalls, increasing the lines broadening via spectral-diffusion effect^{14,97,163}. A potential growth strategy to suppress such parasitic $\text{InAs}_x\text{P}_{1-x}$ radial growth is by including in-situ HCl etching fluxes^{164,165}, although this is not available in our CBE system. Alternatively, since the radial growth rate of the shell is much smaller than the axial growth rate of the QD, thinner QDs could be used to reduce shell formation. Panels (f) and (g) show two STEM images of a 3 nm-thick QD of $\text{InAs}_{0.88}\text{P}_{0.12}$ and pure InAs, respectively. Here, no parasitic $\text{InAs}_x\text{P}_{1-x}$ shell is observed via STEM nor at TEM-EDX line scan (panel h), meaning that the shell is not present or it has a thickness lower than the TEM resolution (>1 nm). Figure 4.3.2 (i) reports a TEM image confirming the absence of structural defects around the QD, a consistent feature of all the ZB NW-QD samples presented in this thesis.

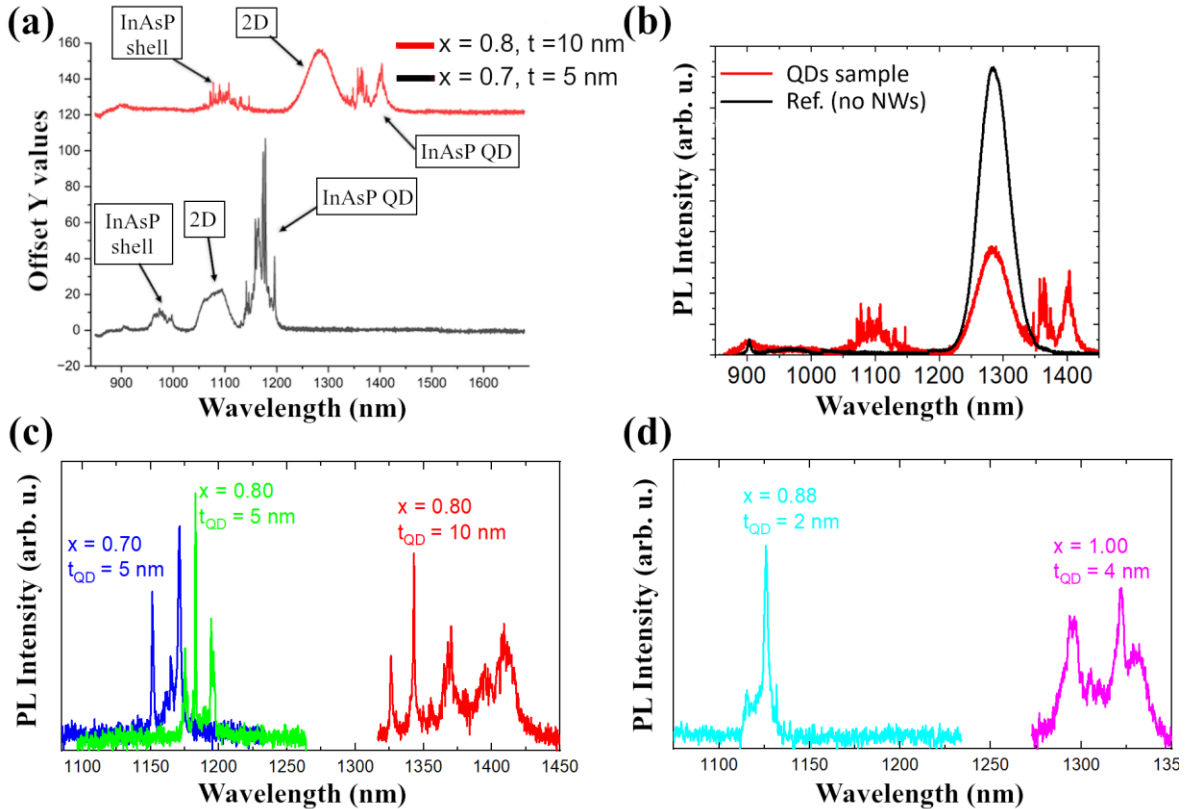
4.4 Optical characterization of the NW-QD tunability

To investigate the emission tunability of the NW-QD samples, μ -PL have been performed both on ensembles of as-grown NW samples and on NWs mechanically transferred onto Si substrates with markers. In Figure 4.4.1 (a), μ -PL spectra from ensembles of as-grown NWs are shown for two representative samples: $\text{InAs}_{0.80}\text{P}_{0.20}$ 10 nm-thick QD (red curve) and $\text{InAs}_{0.70}\text{P}_{0.30}$ 5-thick QD (black curve). The ensemble emission exhibits three distinctive features:

- (i) QDs emission (right side of the spectrum). Given the measured sample average density of ~ 0.9 NWs/ μm^2 and the μ -PL excitation beam spot size of ~ 2 μm , each spectrum contains emission from more than one QD emitter.
- (ii) Broad emission band from the $\text{InAs}_x\text{P}_{1-x}$ 2D layer grown on the substrate. This is confirmed in Figure 3.4.1 (b), which compares the emission of a NW-QD sample (red curve, $x = 0.80$ and QD thickness of 5 nm) with that of a dummy InP substrate grown under identical conditions but without catalysts, leading exclusively to 2D growth (black curve). Both show a band centered at ~ 1280 nm.
- (iii) Higher energy peaks, likely related to the emission from the parasitic radial $\text{InAs}_x\text{P}_{1-x}$ shell.

To demonstrate the emission tunability as a function of the QD features, single QDs are measured by mechanically transfer the NWs to a Si substrate with gold markers, allowing us to isolate and identify single emitters. Figure 4.4.1 (c) shows the emission detected from single NWs with different compositions (blue and green curves) and thicknesses (green and red curves). As expected, increasing either the QD As content or its thickness results in a red-shift of the emission: in the first case due to changes in the QD bandgap material, and in the second case due to quantum size effects. Notably, for $x = 0.8$ and 10 nm thick QD the emission reaches the second telecom O-band window and even extends into the E-band, highlighting the potential of these nanostructures for nanophotonic applications. In panel (d), analogous results are shown for thinner QDs without the parasitic InAs_xP_{1-x} shell discussed in the previous section. Here, a similar spectral tuning is observed, with single-QD emission ranging from slightly above 1.1 μm up to about 1.3 μm of the second telecom window, achievable by increasing the As content up to $x =$

Figure 4.4.1 μ -PL spectra at 4K of NW-QDs. (a) spectra measured from as-grown ensemble of NW-QDs with $x = 0.80$ and 10 nm thickness (red curve) and $x=0.80$ and 5 nm thickness (black curve), showing three different contributions from the InAsP shell, the 2D growth and the InAsP QD; (b) a comparison between a dummy 2D sample (black curve) grown in the same growth conditions of the NW-QD ensemble (red curve) with $x = 0.80$ and 10 nm of thickness; (c) spectra from QD with As content of $x = 0.70$ and 5 nm thickness (blue), $x = 0.80$ and 5 nm thickness (green) and $x = 0.80$ and 10 nm thickness (red); (d) spectra from QDs with $x = 0.88$ and 2 nm thickness (light blue) and $x = 1.00$ (pure InAs) and 4 nm thickness.



0.88 or even to pure InAs. In the case of pure InAs, O-band emission can be reached for almost 2-times thinner QDs compared to the 10 nm-thick QD and $x = 0.80$, with a thickness in the range of 4 nm, providing stronger energy quantization and better isolation of single QD states and related optical transitions. In the reported spectra, spectral diffusion effects dominate the emission linewidth, with a typical line broadening on the order of hundreds of μeV , exceeding the spectral resolution of the experimental setup (20 μeV). Another observation is the presence of few emission lines per QD spectrum, even at the lowest excitation powers. This behavior is common for large-size QDs, such as those studied here^{166–168}. They can originate from either emission of other excitonic complexes (like biexciton or charged complexes) or exciton excited states. For InP-based QDs of comparable dimensions, both mechanisms are consistent with the line separations observed.¹⁶⁹

By tuning the QDs features, based on the presented results, it is possible to tune the wavelength of the emission to the third telecom window, up to 1560 nm. Figure 4.4.2, shows the spectrum obtained from a QD with 10 nm of thickness and $x = 0.87$. Different colours corresponds to different excitation powers. Notably, emission in the Telecom C-

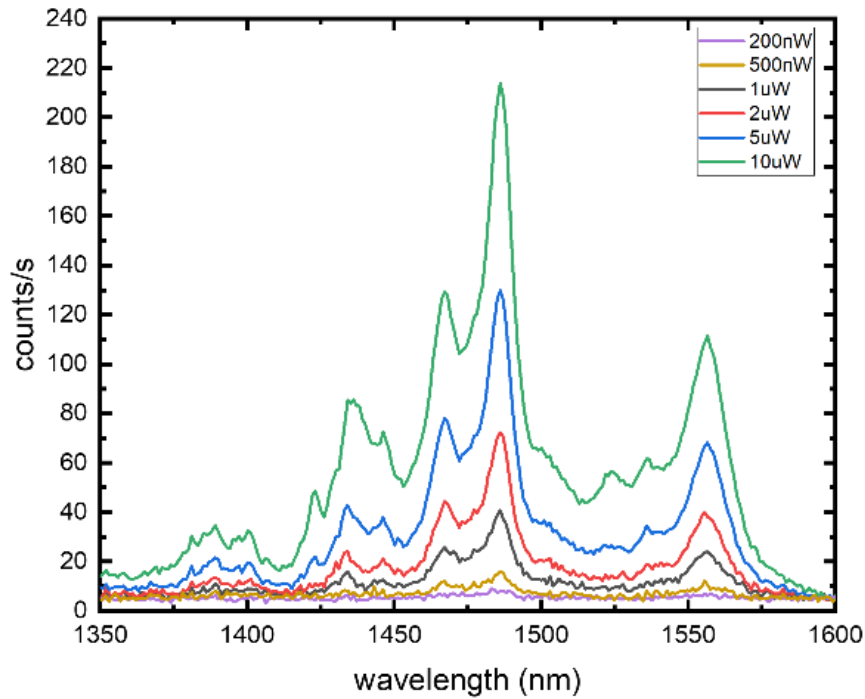


Figure 4.4.2: Power serie made on a sample with 10 nm-thick QDs and $x = 0.87$. The QD features tuning allows to have emission in the Telecom C-band, up to 1560 nm.

band is exhibited by these QDs. The NW-QDs of the spectra in Figure 4.4.2 have integrated a waveguide, which will be discussed in detail in the next chapter.

4.5 Summary and conclusions

In this chapter, we reported the growth, structural analysis, and optical characterization of $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP nanowires along the $\langle 100 \rangle$ direction. A systematic optimization of the InP NW stems growth parameters allowed to achieve nearly untapered morphology of the NWs with a defect-free zincblende structure. The subsequent integration of $\text{InAs}_x\text{P}_{1-x}$ QDs within the NW cores demonstrated the feasibility of controlling both QD thickness and composition, enabling fine-tuning of the bandgap and quantum confinement. High-resolution TEM analyses confirmed the crystal phase purity of the QDs. For larger QDs, parasitic $\text{InAs}_x\text{P}_{1-x}$ shell growth is observable at the NW sidewalls, which can be reduced by a decrease of the QD thickness, exploiting the difference between the radial and axial growth rate. μ -PL measurements highlighted the strong tunability of the emission wavelength through the adjustment of QD dimensions and As content, allowing to reach emission in the Telecom O- and C-band. The presence of spectral diffusion and multiple emission lines per QD is discussed.

Overall, the results presented in the chapter establish a robust growth approach for ZB $\text{InAs}_x\text{P}_{1-x}$ NW-QDs with tailored emission properties in technologically relevant wavelength ranges. The demonstrated structural quality and spectral tunability pave the way for the development of NW-based nanophotonic and quantum devices operating in the telecom regime and grown along the industry-standard substrate orientation.

Chapter 5: Enhancing photon extraction through optimized waveguide for ZB InAsP/InP NW-QDs emitting in telecom range

Introduction

In the previous chapter, the growth of ZB InAs_xP_{1-x} NW-QDs with high crystalline quality and tunable emission wavelengths within the telecom O- and C-bands was demonstrated. However, all measured NW-QDs exhibited relatively low brightness, with average photon count rates of only a few hundred counts per second across the measured samples. In the literature, achieving efficient emission at telecom wavelengths from NW-QDs has proven to be challenging, as a dramatic reduction in brightness is typically observed when extending the emission wavelength toward the telecom range. Detectable signals are often reported only for structures featuring optimized waveguide geometries^{13,15,127}. This loss of brightness has been attributed to several mechanisms, including emission blinking phenomena and, more importantly, to the increase in the QD aspect ratio ($t_{\text{QD}}/D_{\text{QD}}$) required to achieve longer emission wavelengths. In SK-QDs, the strong quantum confinement and low aspect ratio ($t_{\text{QD}}/D_{\text{QD}} \sim 0.1$) result in a splitting between the heavy-hole (HH) and light-hole (LH) valence-band states, yielding a HH-dominated ground state¹⁷⁰. Atomistic tight-binding calculations for InAs/InP QDs have shown that when the aspect ratio increases to around 0.8, strain redistribution within the QD induces a transition from HH to LH-dominated ground state¹⁷⁰. In WZ NW-QDs, where the catalyst diameter is typically constrained below 20 nm to maintain crystal purity, aspect ratios of about 0.4 are commonly reported for telecom emission^{13,127}. Thus, the QD ground state is expected to exhibit a linear combination of HH and LH levels, resulting in excitons with both perpendicular and parallel polarizations^{170–172}. Only the perpendicular ones

efficiently couple to the fundamental HE_{11} guided mode, while the parallel ones emit radially and are poorly collected by standard optical setups, ultimately reducing the extraction efficiency. The ZB NW-QDs presented in this thesis are not subject to the stringent catalyst diameter constraints of the WZ NWs. The typical aspect ratio of ~ 0.2 for these ZB QDs emitting in the telecom range lies between SK-QDs and conventional NW-QDs. This fact likely explains the detectable emission at telecom wavelengths even in absence of an optimized waveguide presented in the previous chapter, partially mitigating the polarization mismatch issue. Nevertheless, further enhancement of brightness requires engineering an efficient waveguide around the QD. Both theoretical¹²⁵ and experimental studies^{127,129} have demonstrated that growing an InP shell with an optimized geometry enables optical mode confinement and adiabatic photon funnelling along the NW axis, thereby significantly improving the light extraction efficiency. Conventionally, such waveguides are realized via a combined SAE-VLS¹²⁹ approach. With this method, the substrate is pre-patterned through lithography and etching to define nanoscale holes in a dielectric mask (SiO_2 or SiN) prior to the growth. A gold catalyst droplet is positioned at the center of each hole via a self-aligned lift-off process. The subsequent growth proceeds in two stages: first, axial VLS growth forms the NW core containing the QD, second, the radial growth is enhanced to form the surrounding InP shell, with the final NW diameter determined by the mask hole size. Although this approach allows precise control and scalability, it involves a pre-growth and time-consuming substrate preparation.

In this chapter, an alternative approach for waveguide engineering that relies solely on the VLS growth mode is investigated, thereby avoiding any pre-patterned substrate and simplifying the fabrication process. Controlling the interplay between simultaneous axial and radial growth is non-trivial, requiring a detailed understanding of how the growth parameters influence the final NW morphology. Section 5.1 discusses the typical morphology observed in our samples. Section 5.2 presents Finite-Difference Time-Domain (FDTD) simulations based on these geometries to identify the most efficient waveguide designs. Section 5.3 provides a systematic experimental study on how the waveguide morphology depends on the growth conditions. Section 5.4 reports the optical characterization and validates the effectiveness of the proposed approach. Finally, Section 5.5 summarizes the main findings.

The FDTD simulations and optical characterizations were performed in collaboration with the group of Prof. Sęk at Wrocław University of Science and Technology, in Poland. The results presented in this chapter have been published in Ref. 17.

5.1 ZB NW morphological evolution with length and typical waveguide geometry

For all the NW-QD samples investigated in this chapter, the InP waveguide shell was grown using the same NW *core* as a template. The NW core is obtained employing the growth protocol discussed in Chapter 4, resulting in InP NWs with a total length of approximately ~ 1100 nm and embedding a (10 ± 2) nm-thick $\text{InAs}_{0.88}\text{P}_{0.12}$ QD. As demonstrated in Chapter 4, these QD features enable emission in the third telecom window, up to 1560 nm. All the samples have a low NW density of $\sim 10^6$ NWs/cm², which allows for single-NW optical characterization. To facilitate navigation on the substrate during the μ -PL measurements, SiO₂ alignment markers are fabricated on the substrate prior to the colloid deposition, as explained in Section 3.1. The growth of the InP shell around the NW core - referred to as the *waveguide growth step* - is discussed in the following sections, focusing on how the growth conditions influence the resulting shell morphology. A schematic of the growth procedure is shown in Figure 5.1 (a). The first step (NW core growth) follows the process detailed in Chapter 4, while the second step (waveguide shell growth) represents the focus of this chapter. In the remainder of this section, we focus on the typical morphology observed in our NWs and on its evolution as a function of the total NW length. Figure 5.1 (b-e) reports 45°-tilted SEM images of representative NWs from ensembles with an average total length of: (290 ± 60) nm, (690 ± 130) nm, (1440 ± 20) nm, and (1450 ± 90) nm, respectively. In particular, panel (d) shows a typical NW core prior to the InP shell growth, while panel (e) shows an example of a typical final sample, with an InP shell grown for 50 minutes at the QD temperature employing TMIn and TBP of 0.40 Torr and 1.60 Torr, respectively. As the NW length increases, a characteristic three-segment morphology develops, highlighted with false colours in panel (e) and schematically illustrated in the inset. The morphology consists of three distinct segments:

- (i) *Cuboid segment (base)*: an untapered region at the NW bottom with a constant side length D_c . This segment will be referred to as “cuboid”.
- (ii) *First tapered segment*: located above the cuboid, this region exhibits a monotonic decrease in side length from D_c to D_2 , with total length L_2 .
- (iii) *Second tapered segment*: the uppermost region, characterized by a different tapering angle compared to the previous one, with a bottom side length D_2 , a top side length determined by the catalyst nanoparticle, $D_{NP} = (48 \pm 4)$ nm, and length L_3 .

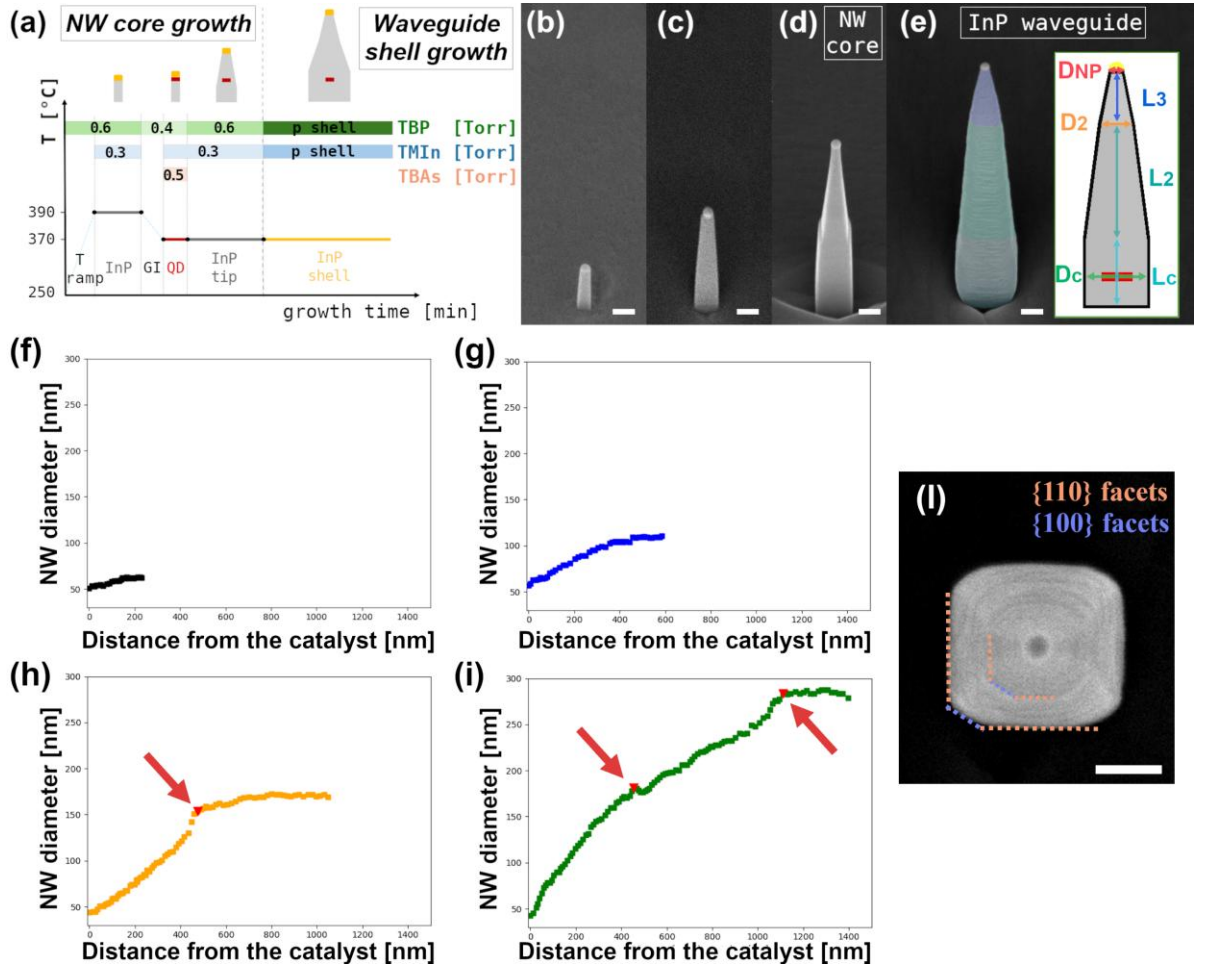


Figure 5.1: (a) Scheme of the growth protocol employed for the NW-QD samples, divided in the NW core growth and the InP shell growth. For each growth step, the TBP, TMin and TBAs line pressures (in Torr) are reported in the green, blue and orange boxes, respectively. A schematic of the NW growth is also reported at the graphic top; (b-e) 45°-tilted side view SEM images of a representative NW of different lengths. In particular, the average total length of the ensemble is: (b) (290 ± 60) nm; (c) (690 ± 130) nm; (d) (1140 ± 20) nm; and (e) (1446 ± 94) nm. Here, the three different segments of the NWs are highlighted with fake colours and in the inset, a schematic of the NW morphology with its relevant parameters is represented. Scale bars of panels (b-e) corresponds to 200 nm; (f – i) profiles measured on the SEM images in panels b-e; (j) top-view SEM image of the sample in panel e. {110} facets are highlighted in orange, while {100} facets are highlighted in violet. Scale bar is 100 nm.

This three-segment morphology is consistently observed across all samples with a waveguide grown, resulting from the simultaneous axial and radial growth of the NW. Figures 5.1 (f-i) show the NW side length profiles extracted from the SEM images in panels (b-e), respectively. The profiles are obtained using ImageJ software¹⁷³. On each NW, the NW side length is measured at regular intervals of about 10 nm along the NW axis, starting from the catalyst nanoparticle and moving towards the NW base. At each measurement point, both the NW side length and its distance from the catalyst is recorded, obtaining the side length profile along the entire NW length shown in panels (f-i). The development of the three-segment morphology with NW total length is clear, starting from an almost untapered NW in panel (f), and with the development of the three-segments in panel (i). The transition points between the three segments are highlighted with red points and arrows. Complex NW morphologies have already been reported in literature^{74,174} and the modelling of the growth dynamic remains non-trivial, with complex interplay between the simultaneous axial and radial NW growth. The three-segment morphology observed in these ZB NWs likely arises from variations in the competition between the axial and radial growth at different heights along the NW axis, driven by the diffusion behaviour of In adatoms. The cuboid segment has been previously observed in InP NWs^{175,176}, and in other materials⁷⁶, and has been attributed⁷⁷ to a region of the NW located farther from the catalyst than the typical diffusion length of In adatoms on the sidewalls. Consequently, the radial growth of the cuboid proceeds primarily through direct impingement of In adatoms on the NW sidewalls and diffusion of In adatoms from the substrate. In our case, the NW cuboid sidewalls are {110} family facets, with just a minor overgrowth of the {100} facets, as shown in the top-view SEM image in Figure 5.1 (l), with highlighted the two types of family facets in orange and violet, respectively. Typically, in literature a single segment is observed on top of the cuboid. Conversely, the presence of two different tapering segments is characteristic of our NWs and, to the best of my knowledge, has never been reported in literature. These segments are located within the diffusion length of the In adatoms on the sidewalls. Thus, In adatoms impinging on NW sidewalls within these two regions can either diffuse toward the droplet and contribute to the NW axial growth, or incorporate on the NW sidewalls, contributing to the radial growth. The presence of two distinct tapering angles suggests a complex growth mechanism in which the balance between axial and radial contribution varies with the NW height. Similar abrupt morphological tapering transitions, leading to “pencil shaped”

NWs, have been reported in other NW materials¹⁷⁴ and are often modelled in terms of a step-flow growth mechanism^{73,75–77}. While a detailed modelling of the growth of our NWs is beyond the scope of the present chapter and surely needs more insights about the exact growth dynamics via in-situ TEM or lamellas studies, it is possible to observe from Figure 5.1 (l) a gradual facets evolution along the NW axis, from mainly $\{110\}$ facets in the cuboid segment, to both $\{110\}$ and $\{100\}$ facets of equal side length toward the NW top, resulting in an octagonal NW cross section. Such transition in the sidewall facets along the height of ZB InP NWs is expected to affect the In adatoms due to the different facet polarities^{68,106}, which in turns influences the nucleation probability¹⁷⁷ and adatom diffusion length⁶¹. From these experimental findings, two key points emerge. The NW morphology is length-dependent, requiring comparison to be made between ensembles of NWs with similar average length. Second, a systematic study aiming at tuning the geometrical parameters (L_c , D_c , L_2 , D_2 , L_3) is essential to achieve a well-defined and efficient InP waveguide shell for enhanced optical performance.

5.2 Finite-Difference Time-Domain (FDTD) waveguide modelling

Based on the experimentally observed morphology of the NW-QDs, the three-segment geometry can be used as an input for Finite-Difference Time-Domain (FDTD) simulations, with the aim of identifying the optimal geometrical parameters - L_c , D_c , L_2 , D_2 , L_3 – required to achieve efficient waveguiding and to maximize the light extraction efficiency into the numerical aperture (NA) of the collection optics used in the μ -PL setup (NA = 0.4). The results obtained from the FDTD simulations serve as benchmarks for the subsequent growth optimization of the InP shell. All simulations are carried out using the commercial software *Ansys Lumerical*¹⁷⁸ and the geometry is optimized for an emission wavelength of $\lambda = 1.50 \mu\text{m}$.

The first step consists in finding a preliminary value of the cuboid lateral side length at the QD height (D_c). To this end, the NW geometry is initially modelled as an infinitely long, untapered, square-based InP NW, with a side length D_c and modelled in 2D. The QD is simulated as a point source electric dipole placed on the NW z axis and polarized along the x direction. Perfectly Matched Layer (PML) absorbing boundary conditions are

applied for the computational domain. Furthermore, planar monitors are placed around the NW, normal to x, y and z directions, to evaluate the dipole emission collected along each direction. To assess the optical confinement for single mode propagation along the NW, three quantities are investigated:

- (a) *The spontaneous emission rates into the fundamental waveguide mode* (Γ_{11}), obtained by dividing the transmitted power through the monitors by the Purcell factor.
- (b) *The leaky modes* (γ), which constitute the radiation losses in the planar direction and are calculated as the sum of the transmitted power through the x and y monitors.
- (c) *The β -factor*, i.e. the coupling efficiency into a guided optical mode, defined as:

$$\beta = \frac{\Gamma_{11}}{\Gamma_{11} + \gamma}.$$

Figure 5.2 (a) shows the calculated normalized spontaneous emission rates as a function of D_c . The best confinement of the fundamental mode and the lowest radiation losses are achieved for $0.22 < \frac{D_c}{\lambda} < 0.26$, in good agreement with previous reports on NW-QD systems emitting at shorter wavelengths¹²⁵. For smaller D_c , the guided mode is weakly confined within the NW, strongly leaking out, and strong increase in the radiation losses γ occurs. For larger D_c , the confinement gets weaker and after exceeding the cut-off value the structure becomes multimodal, decreasing the coupling into the fundamental mode. Because of different spatial distribution of the electromagnetic field for the different modes, e.g., with the field maximum near the NW edge, the radiation loss increases.

In the next step, the more realistic NW geometry observed experimentally (see Figure 5.1 (e)) is taken into account to fine-tune the design and identify the geometrical parameters critical to maximize photon extraction. The NW is thus modelled in 3D with a square cross-section, placed on a InP substrate. D_c is set to the optimal value of 330 nm, while D_{NP} , L_2 and L_3 are set to 50 nm, 620 nm, and 350 nm, respectively. Suitable symmetry boundary conditions are applied to reduce computational volume. The gold catalyst droplet, due to its sub-wavelength size, results in negligible optical perturbation and it is thus neglected. The extraction efficiency in the upwards axial direction is evaluated as

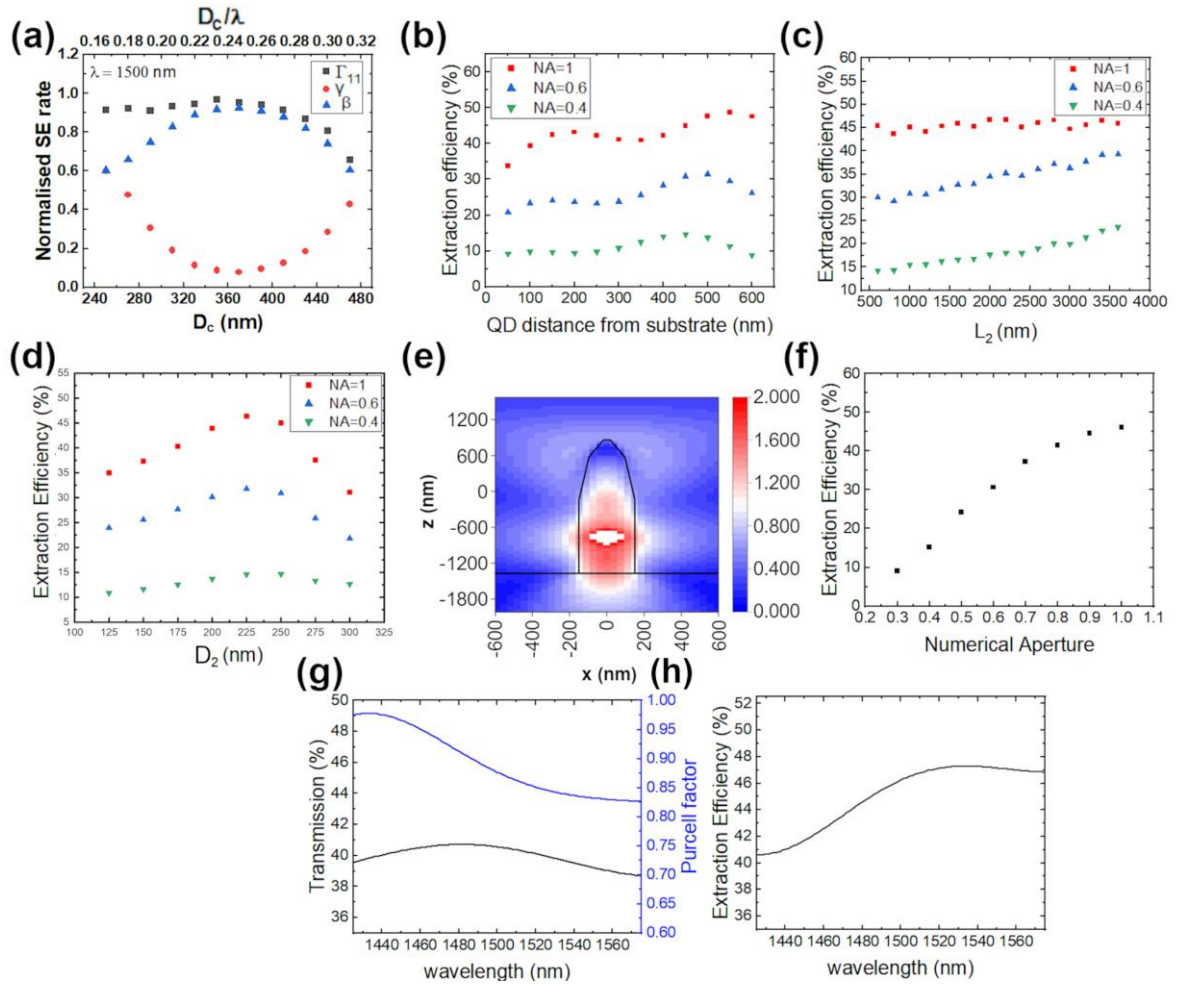


Figure 5.2: (a) Calculated normalized spontaneous emission rates of a radial dipole embedded on axis, in an infinitely long and square-base InP NW. Γ_{11} (black squares), γ (red dots), and β (blue triangles) are presented as a function of NW side length D_c (bottom axis) and ratio between D_c and emission wavelength (top axis); (b) Extraction efficiency as a function of QD position along the NW axis within different NA of collection optics for optimized tapered NW geometry; (c) Extraction efficiency as a function of L_2 withing different NA of collection optics for optimized tapered NW geometry; (d) Electric field distribution (colour coded) from dipole emission in a tapered NW geometry; (e) Extraction efficiency as a function of NA of collection optics for tapered NW with optimized geometry parameters; (f) Transmitted power through a planar monitor above the optimized tapered NW (corresponding to NA = 1) – black solid line (left vertical axis), and Purcell factor values (blue line, right vertical axis) for different dipole emission wavelengths; and (g) Extraction efficiency as a function of the dipole emission wavelength in optimized tapered NW.

the Purcell-factor normalized transmission through a planar monitor placed above the NW. Different NA values of the collection optics are emulated by cutting out the corresponding areas from the far-field projection. Figure 5.2 (b) presents the extraction efficiency as a function of the QD position along the NW axis, placing the emitting dipole at the center of the square base cross section and changing its height with respect to the substrate. The optimal QD position for NA= 0.4 is found at 450 nm from the substrate, corresponding to the maximum of the guided mode electric field (see Figure 5.2 (d)). The corresponding Purcell factor is close to 1, as seen in Figure 5.2 (a). The second NW segment plays a dominant role in light outcoupling: increasing its L_2 enhances emission

directionality and, consequently, extraction efficiency, as presented in Figure 5.2 (c). The bottom part of the NW, characterized by $\frac{D_c}{\lambda} = 0.22$, lies at the lower limit of the optimal D_c range for confinement. For the cost of slightly worse confinement, the second segment of the NW taper angle can be decreased while keeping D_2 small enough to minimize scattering from the top facet, which enhanced extraction efficiency within small NA. The third segment, arising from the presence of the catalyst nanoparticle, is optically inactive, and minimizing its length L_3 is beneficial since the electric field does not enter this segment, as shown in Figure 5.2 (d). Figure 5.2 (e) shows the extraction efficiency as a function of the NA for the NW with fully optimized geometry. Overall, a maximum photon extraction efficiency of 46% is achieved for high NA, while for NA = 0.4 (the typical experimental condition) the efficiency is reduced to 15%. The Purcell factor, shown in Figure 5.2 (f), remains slightly below 1 due to the imperfect D_c value, as mentioned earlier, and due to the scattering from the third segment of the NW. Importantly, the extraction efficiency remains high for a certain range of emission wavelengths, as shown in Figure 5.2 (g). Spectrally broad extraction function is practically beneficial as it does not require additional fine tuning of the QD emission as long as it falls into the high extraction range.

In summary, the FDTD simulations indicate the following optimal geometrical parameters for efficient waveguiding at telecom wavelengths: $D_c = 330$ nm, $L_c > 450$ nm, mainly to provide a uniform QD environment of the shell, $L_2 = 620$ nm, $D_2 = 250$ nm, and $L_3 = 350$ nm or smaller. The QD should be positioned at 450 nm from the NW base to coincide with the maximum of the optical mode electromagnetic field within the NW waveguide.

5.3 Dependence of the waveguide morphology from the growth parameters

From the results presented in Section 5.2, it is clear that the waveguiding performance of the NWs is mainly determined by the value of D_c , with the optimum found at $D_c = 330$ nm for an emission wavelength of 1500 nm, and by the position of the QD along the NW axis. While the latter can be easily controlled during the NW core growth, by simply

choosing the growth time of the first InP segment prior to the QD growth, the side length D_c is strongly correlated with other morphological parameters of the NW waveguide. Moreover, achieving high photon extraction efficiency requires proper control of the tapering in the second NW segment. To enable a quantitative comparison of the morphology across different samples, we introduce two dimensionless waveguide parameters that capture the most relevant aspects of the NW geometry:

- ϵ_{D_c} , it is the relative percentage deviation of D_c from the target value $D_c^{target} = 330$ nm. It is defined as:

$$\epsilon_{D_c} = \frac{D_c - D_c^{target}}{D_c^{target}} \cdot 100 \quad (5.1)$$

It provides a direct measure of how much the cuboidal segment lateral side length deviates from the optimal value for waveguiding. A value of $\epsilon_{D_c} = 0$ corresponds to the ideal NW geometry where D_c is equal to the target value $D_c^{target} = 330$ nm.

- t_2 , the tapering parameter of the second NW segment, primarily affecting the light extraction efficiency of the waveguide. It is defined as:

$$t_2 = \frac{1}{2} \cdot \frac{D_c - D_2}{L_2} \quad (5.2)$$

t_2 is zero for an untapered segment, negative for divergent tapering, and positive for convergent tapering. Substituting the optimal geometrical parameters obtained from the FDTD simulations yields t_2 optimal values in the range 0.020 (for $L_2 = 2$ μm) to 0.065 (for $L_2 = 620$ nm), with smaller values being preferable.

For each analyzed sample, these two parameters are determined as follows. From side-view SEM images of individual NWs, the lateral side length profile of the NW is extracted as a function of the distance from the catalyst droplet, an example of which has been already presented in Figure 5.1 (i). The transition points between the three morphological segments are identified from the change in slope of the profile, allowing direct determination of D_c , L_2 and D_2 . The procedure is performed on at least 15 NWs per

sample, and the corresponding mean values and standard deviations are calculated, as well as ϵ_{D_c} and t_2 .

After determining the relevant quantities, the remainder of this section focuses on the growth of the InP shell, using the NW core as a template. Since the NW morphology is closely related to the diffusion length of In adatoms along the sidewalls, the InP shell geometry is investigated as a function of the growth parameters that can influence adatom mobility and incorporation: InP shell growth temperature, V/III ratio, and total TMIn flux.

5.3.1 Waveguide growth dependence on growth temperature.

The temperature is an important growth parameter that acts on both the radial and the axial growth of the NW by changing the group III adatom diffusion. In particular, it has been observed that a decrease in temperature typically leads to an enhancement of the radial growth rate of the NW, while higher temperature could lead to thermal decomposition of the NW facets in ZB InP NWs growth along the $\langle 100 \rangle$ direction, with a change in the cross-sectional shape of the NW⁶⁸. Since the aim is to enhance the radial growth for the waveguide and to avoid such thermal decomposition, InP shell experiments are conducted by decrease the temperature of the InP shell growth compared to the QD growth temperature. Figure 5.3.1 shows two different samples grown with an InP shell of 50 minutes using TMIn and TBP line pressures of 0.40 Torr and 1.60 Torr, respectively, at different temperatures. Panel (a) shows a sample in which the temperature is decreased by 20 °C after the growth of the core with a 5 minutes-long linear ramp, while linearly ramping TMIn and TBP line pressures from the ones of the core to the ones of the shell. The clear effect is a destabilization of the catalyst nanoparticle, leading to a not straight NW growth. By decreasing the temperature of 10°C compared to the QD, as in the sample of panel (b), kinking of the NW is observed, leading again to not straight

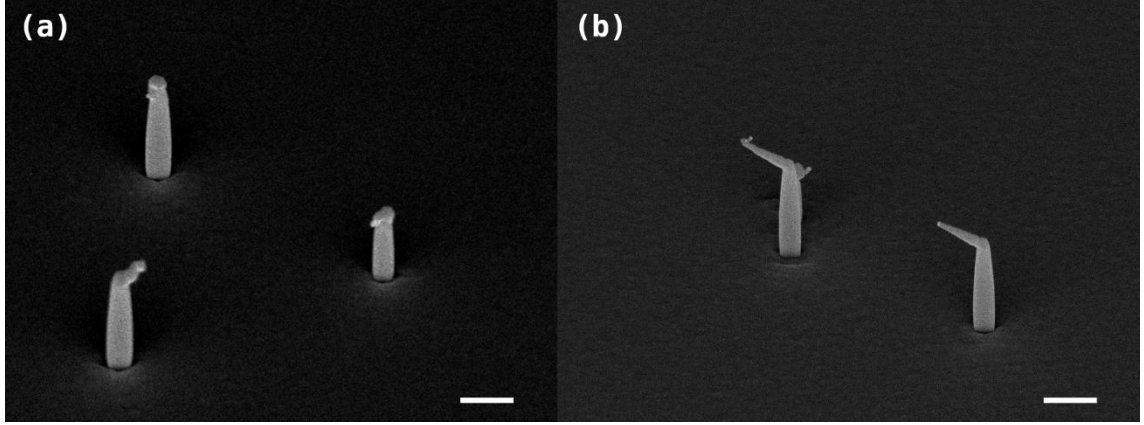


Figure 5.3.1: 45°-tilted side-view SEM images of samples with the InP shell grown at a temperature: (a) lower than 20 °C compared to the QD growth and (b) lower than 10°C compared to the QD growth. In both images, the scale bar is 500 nm.

growth. This suggest that the growth temperature window for these samples is quite narrow, and the InP shell growth temperature must be kept equal to the QD growth temperature.

5.3.2 Waveguide growth dependence on V/III ratio

To investigate the effect of the V/III ratio on the waveguide morphology, four samples are grown under different V/III ratio conditions for the InP shell. In each case, a 50 minutes InP shell is grown after the NW core by keeping TMIn at 0.40 Torr, while varying TBP line to achieve V/III ratios of: 2.00, 3.00, 4.00, and 5.00. Figure 5.3.2 presents representative 45°-tilted SEM images of single NWs from each of these samples in panels (a), (b), (c), and (d), respectively. The dependence of t_2 , ϵ_{Dc} and L_3 from the V/III ratio are reported in Figure 5.3.2 (e). No strong dependence on the V/III ratio is observed, with t_2 remaining close to the optimal range (highlighted in green in the graphic), while D_c deviates by ~20% below the target value for all the investigated conditions and L_3 being constant. Panel (f) reports the axial and radial growth rates of the InP shell, which appear unaffected by the V/III ratio. This indicates that, under the presented growth conditions, the overall growth regime is mainly limited by the TMIn transport rather than by the group V precursor supply. For all the V/III ratios investigated, the cuboidal base of the NWs maintains a square cross-section bounded by $\{110\}$ facets, with only minimal overgrowth of the $\{100\}$ facets, which remains comparable across all samples. This

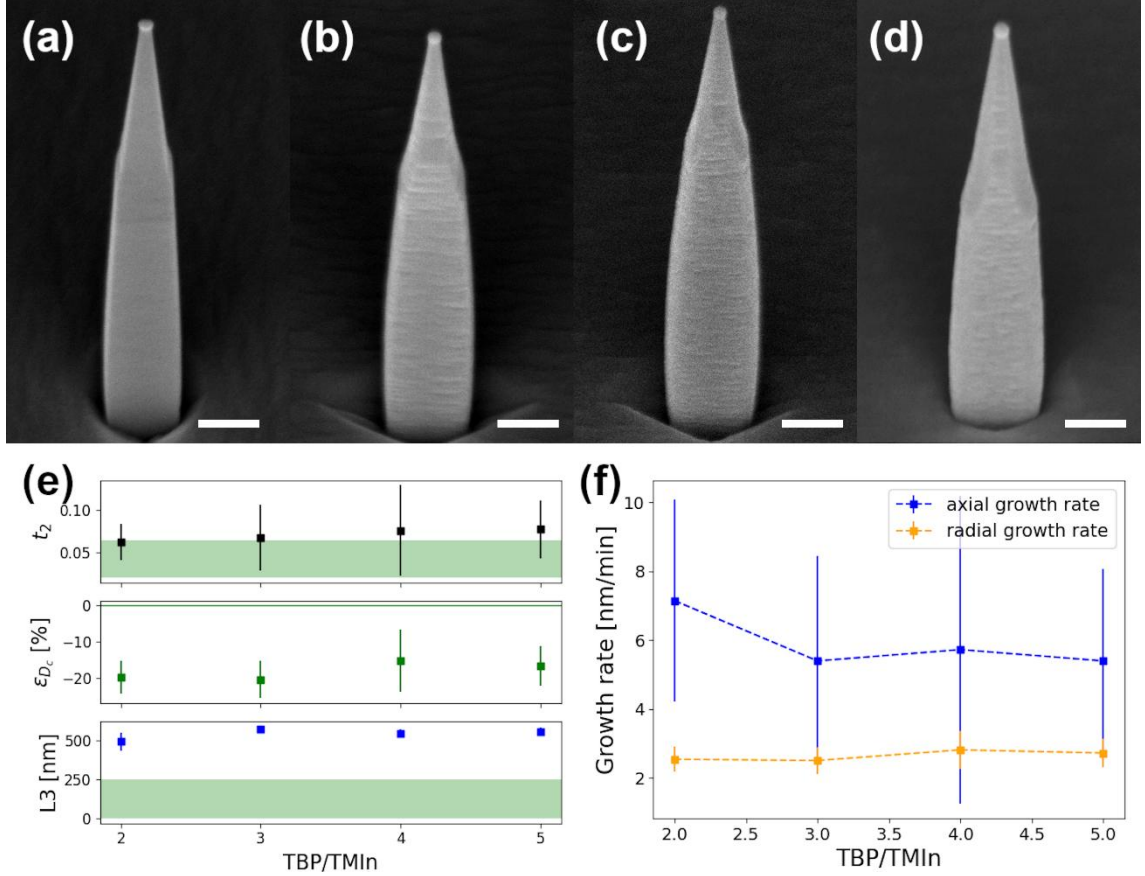


Figure 5.3.2: 45°-side view SEM images of the samples with an InP shell grown at TBP and TMIn line pressures of: (a) 2.0; (b) 3.0; (c) 4.0; and (d) 5.0. Scale bars in panels (a-d) are 200 nm; (e) Dependence of the average t_2 , ϵ_{Dc} , and L_3 from the V/III ratio. In green, the optimal value ranges from FDTD calculations are highlighted; (f) Axial (blue) and radial (orange) growth rates dependence on the V/III ratio.

observation is consistent with the results reported in Ref.179, but differs from Ref.68, where a change in the cross-sectional morphology of $\{100\}$ -faced NWs was observed – likely due to the use of a higher range of V/III ratios allowed in the employed MOVPE. Since the V/III ratio does not exhibit a significant influence on the NW morphology within the explored range, it is fixed at 4.00 for the subsequent investigation of the effect of the total TMIn line pressure on the NW morphology.

5.3.3 Waveguide growth dependence on TMIn line pressure

Since the growth regime is found to be mainly limited by the group-III precursor supply, the total TMIn line pressure is expected to have a strong impact on the balance between

axial and radial growth rates during NW formation. To investigate this effect, a set of samples was grown at fixed V/III ratio of 4.00 while varying TMIn line pressure. Figure 5.3.3.1 shows 45°-tilted SEM images of representative NWs from samples with an InP shell grown under TMIn line pressures of 0.20 Torr, 0.30 Torr, 0.40 Torr, 0.50 Torr, and 0.60 Torr, reported in panels (a-e), respectively. All samples are grown to have a similar average NW total length of (1400 ± 100) nm, to exclude length-dependent effects. From the SEM images, a clear dependence of the NW morphology on the TMIn line pressure is observed. Increasing TMIn strongly modifies the relative lengths of the L_3 and L_2 segments, with the second segment completely disappearing at the highest TMIn value (panel (e)). This is accompanied by the pronounced and undesired increase of L_3 , as shown in the graph in Figure 5.3.3.1 (f). Moreover, microfaceting of the sidewalls becomes evident at higher TMIn fluxes, consistently with Ref.68. This phenomenon has been attributed to a reduction in the diffusion length of In adatoms under higher precursor fluxes^{180,181}, leading to their incorporation closer to the impinging site and promoting the formation of higher-energy micro-facets. Panel (f) displays the dependence of the waveguide relevant quantities on TMIn line pressure. In particular, the tapering parameters t_2 behaves in a non-monotonic way, with the best value obtained at TMIn line pressure of 0.40 Torr. The non-monotonic trend mainly arises from the competition between the axial growth of segments L_2 and L_3 : while D_c and D_2 increase similarly with TMIn, the axial length L_3 grows exponentially with TMIn, (see Figure 5.3.3.1 (f), in which the red curve is the plot of an exponential fit). At the same time, L_2 decreases due to the overgrowth of L_3 . The interplay between these effects leads to the observed complex trend of t_2 . As expected, the radial growth rate of the cuboidal segment increases with TMIn pressure, resulting from the shorter diffusion length of In adatoms and the enhanced probability of nucleation on the NW sidewalls. At the highest TMIn line pressure, the morphology evolves into a single tapered segment above the cuboidal base, effectively eliminating the distinction of the second segment, although D_c being the closest to the target value for efficient waveguiding for this NW total length. Figure 5.3.3.1 (g) compares the axial growth rate (blue curve) and the radial growth rate (orange curve) at the QD height as a function of the TMIn line pressure. A linear fit provides a first-order estimate of their relative change: decreasing TMIn by 0.10 Torr reduces the axial growth rate approximately 4 times more than the radial one. Figures 5.3.3.1 (h-l) show top view SEM images of the samples grown with TMIn at 0.30 Torr, 0.40 Torr, and

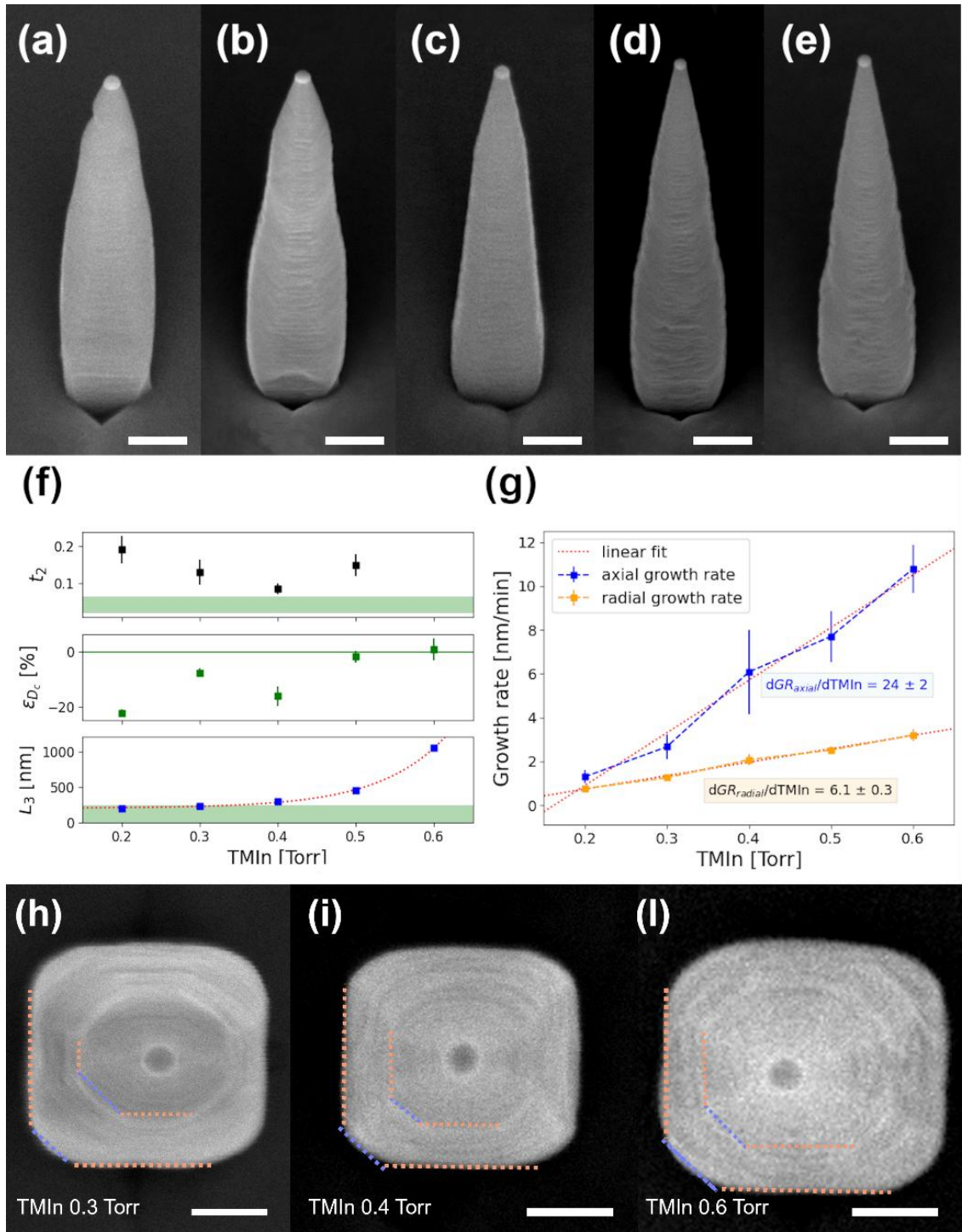


Figure 5.3.3.1: 45°-tilted side view SEM images of representative NWs grown by keeping $V/III = 4$ and employing TMIn line pressure for the shell: (a) 0.20 Torr; (b) 0.30 Torr; (c) 0.40 Torr; (d) 0.50 Torr; and (e) 0.60 Torr. In all the images the scale bar corresponds to 200 nm and the NW length is on average (1400 ± 100) nm for all the samples; (f) Dependence of the average t_2 , ϵ_{D_c} and L_3 on the TMIn line pressure employed for the shell growth. In green, the optimal value ranges for each quantity are highlighted; (g) Axial NW growth rate (in blue) vs. radial growth rate at the QD height (in orange) dependences on the TMIn line pressure employed for the shell growth. Red dotted lines are the linear fits, with which the variations $\frac{dGR_{axial}}{dTMIn}$ and $\frac{dGR_{radial}}{dTMIn}$ of the growth rates with TMIn have been computed; top view SEM images of the sample grown with TMIn line pressure: (h) 0.30 Torr; (i) 0.40 Torr; and (l) 0.60 Torr. $\{110\}$ and $\{100\}$ facets are highlighted in orange and violet, respectively.

0.60 Torr, with $\{110\}$ and $\{100\}$ family facets highlighted in orange and violet, respectively. At lower TMIn line pressure, a more pronounced overgrowth of the $\{100\}$

facets compared to the $\{110\}$ is observed, whereas higher TMIn fluxes stabilize the $\{110\}$ facets along the NW height. The cuboid side facets, however, remain unaffected by TMIn flux. Further insight into these growth modes of the NWs could be achieved by TEM analysis of lamellae extracted at different NW heights, which would help clarify the influence of facet polarity on the final three-segment NW morphology.

From these results, the best InP shell growth condition is identified so far at TMIn = 0.40 Torr and TBP 1.60 Torr, giving the best value for $t_2 = 0.09 \pm 0.01$ and $\epsilon_{D_c} = -0.16 \pm 0.04$, below the target value. This sample will hereafter be referred to as the “*template*” sample. However, as discussed in Section 5.2, the value of D_c is crucial for efficient waveguiding of the QD emission. Therefore, further optimization is required to increase D_c toward its optimal value while maintaining t_2 close to the optimal range.

Two strategies are explored to further improve the waveguide morphology, as schematized in Figure 5.3.3.2 (a). In the first approach (blue arrow), starting from the template sample, the InP shell growth is simply extended under identical conditions (TMIn/TBP = 0.40 Torr/1.60 Torr) for an additional 20 minutes, resulting in an average total NW length of (1640 ± 30) nm. Figure 5.3.3.2 (b) compares the relevant morphological parameters of this extended-growth sample (blue points) with those of the template sample (black points). Representative 45°-tilted SEM images of both NWs are

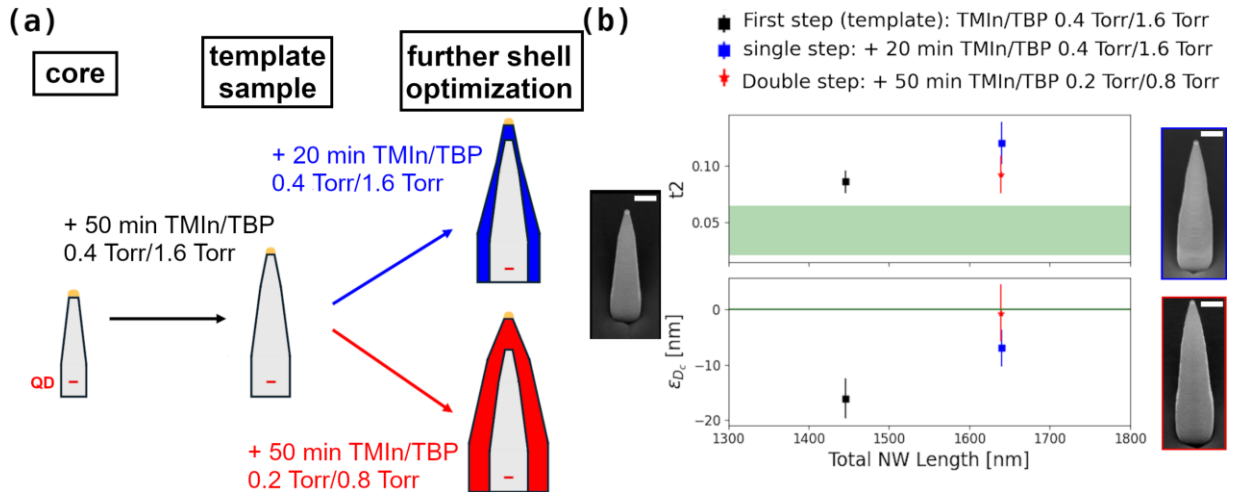


Figure 5.3.3.2: (a) A schematic of the three samples growth; (b) comparison of the waveguide relevant quantities between the template sample (black point), with a sample grown in the same conditions but for longer time (blue point) and a sample grown with the double step approach explained in the main text (red point). A SEM image of the three samples is also reported in the black, blue, and red boxes, respectively (scale bar is 200 nm).

shown in the corresponding insets. In this case, ϵ_{D_c} moves closer to its optimal value, but t_2 largely increases beyond the desired range. The second approach (red arrow in Figure 5.3.3.2 (a)) employs a two-step InP shell growth. After the growth of the template sample, the precursor line pressures are reduced to $\text{TMin/TBP} = 0.20 \text{ Torr}/0.80 \text{ Torr}$ for an additional 50 minutes of growth. The choice of lowering TMin during the second step growth is motivated by the need to promote radial growth, while limiting further axial elongation, as suggested by the growth rate comparison in Figure 5.3.3.1(g). The measured InP shell parameters for this sample are shown in Figure 5.3.3.2 (b) (red points), as well as a representative NW SEM image in the red inset. Compared to the extended-growth strategy (blue spots), the double-step growth approach successfully tunes ϵ_{D_c} to the optimal value $\epsilon_{D_c} = 0$, while keeping t_2 closer to the target range. It must be mentioned that t_2 is 0.11 ± 0.01 , thus slightly above the optimal value. While $D_c = (328 \pm 17) \text{ nm}$ for this sample is in the optimal range and also $L_2 = (628 \pm 58) \text{ nm}$ is the value required from the calculations, the main affecting parameters for the higher value of t_2 is $D_2 = (212 \pm 7) \text{ nm}$, slightly lower than the optimal value. Overall, these results demonstrate that the double-step strategy improves the InP shell morphology but also highlights the potential for further refinement. In particular, a careful tuning of the relative durations of the two shell growth steps should allow the balance of the axial and radial contributions more precisely, ultimately converging toward the fully optimized morphology for efficient light guiding.

5.4 Optical characterization of NW-QDs with different waveguide parameters.

The influence of the waveguide morphology on the optical properties of the NW-QDs is investigated through μ -PL measurements at 10 K. In particular, the following samples are investigated, each characterized by different waveguide parameters:

- The *NW core*, already shown in Figure 5.1 (d). This sample exhibit a small $D_c = (163 \pm 15) \text{ nm}$ (i.e. $\epsilon_{D_c} = -0.50 \pm 0.05$), and a single top segment with a large

tapering angle, resulting from the constrained upper side length imposed by the catalyst nanoparticle and the short tapering length. Representative μ -PL spectra are from a NW of this sample are reported in Figure 5.4 (a).

- The *template sample*, grown with an InP shell in a single step under TMIn and TBP line pressures of 0.40 Torr and 1.60 Torr, respectively, and corresponding to the black points in Figure 5.3.3.2 (b). This sample has $D_c = (277 \pm 17)$ nm, smaller than the optimal value (i.e. $\epsilon_{D_c} = -0.16 \pm 0.04$), and $t_2 = 0.09 \pm 0.01$. Representative μ -PL spectra are displayed in Figure 5.4 (b).
- To assess the effect of an excessively large D_c , a sample is grown under the same conditions of the template but for a longer time (95 minutes), yielding $D_c > D_c^{target}$. The resulting NWs have $D_c = (369 \pm 9)$ nm (i.e. $\epsilon_{D_c} = 0.12 \pm 0.03$) and $t_2 = (0.10 \pm 0.02)$. Representative μ -PL spectra are reported in Figure 5.4 (c).
- The *optimized sample* realized with the double-step growth approach described in Section 5.3.3, corresponding to the red points in Figure 5.3.3.2 (b). This sample has $D_c = (328 \pm 17)$ nm (i.e. $\epsilon_{D_c} = 0.01 \pm 0.05$), $t_2 = (0.09 \pm 0.02)$, values closest to the target design. Representative μ -PL spectra are displayed in Figure 5.4 (d).

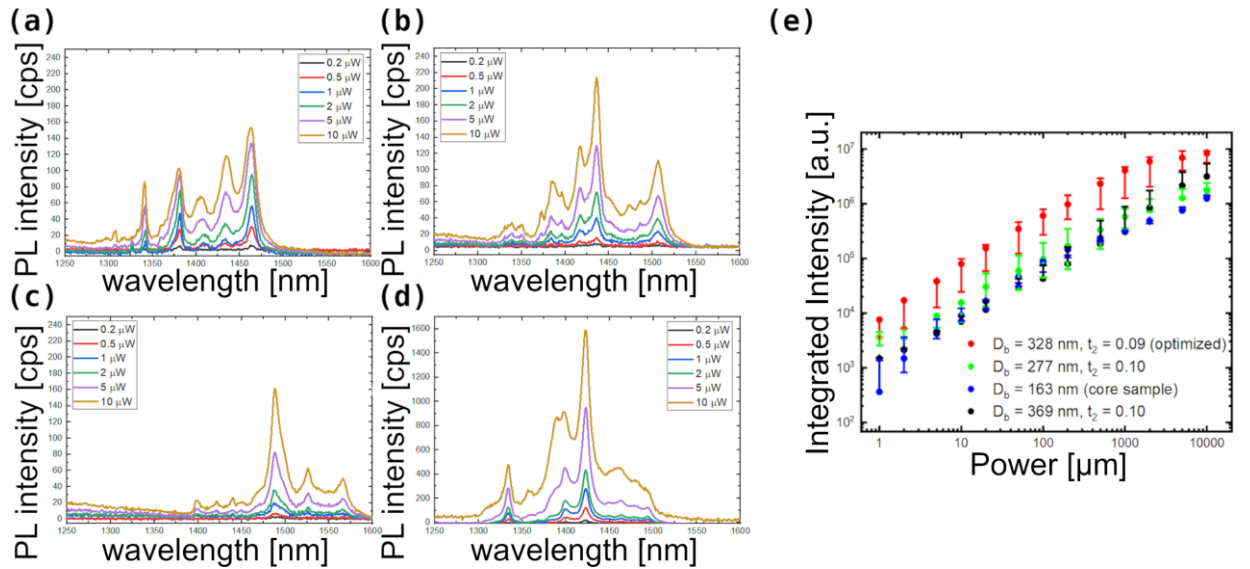


Figure 5.4: μ -PL spectra measured at $T = 10$ K with different excitation powers using 640 nm non-resonant excitation of samples with: (a) $D_c = (163 \pm 15)$ nm, being the core sample; (b) $D_c = (277 \pm 17)$ nm and $t_2 = 0.09 \pm 0.01$, being the template sample; (c) $D_c = (369 \pm 9)$ nm and $t_2 = 0.10 \pm 0.02$; and (d) $D_c = (328 \pm 17)$ nm and $t_2 = 0.09 \pm 0.02$. This is the sample with the optimized InP shell; (e) Integrated intensity of emission as a function of excitation power, for the NW-QDs of panels (a-d). Error bars mark statistical error for measurements on three arbitrary NWs from each sample.

All the spectra exhibit multiple emission lines, confirming three-dimensional carrier spatial confinement within QD potential. Depending on the details of QD height and As content, the emission from these samples can be observed in the range of 1.30 – 1.56 μm and consists of many lines resulting from emission from various excitonic complexes in their ground and possibly excited states. The differences in emission energy between the samples reflect small unintentional variations between QD morphologies, mostly slightly different QD heights that naturally occur from sample to sample during the growth and are also present in the same sample, with an average QD height of (10 ± 2) nm. The full width at half maximum (FWHM) of individual emission lines is on the order of a few meV, which can be attributed to the spectral diffusion due to charge fluctuations around the QD. Optimizing FWHM is beyond the scope of this study, since the focus here is on photon extraction efficiency rather than emission linewidth. To quantitatively compare the waveguide designs in terms of photon extraction efficiency, the integrated emission intensity from a single NW-QD is used as a figure of merit. The integrated emission intensity is obtained by integrating the spectrum numerically in the whole spectral range of NW-QD emission. Multiple NW-QDs (three per sample) are measured to account for statistical variation, and the average value is used. Although this approach does not yield the absolute photon extraction efficiency, it provides a reliable comparison of relative efficiencies between samples. The underlying assumption is that QDs in different samples have approximately the same internal quantum efficiency, supported by the fact that the QD parts of all the structures have identical nominal parameters and growth conditions. An even stronger requirement is typically used in the case of the determination of photon extraction efficiency, where 100% internal quantum efficiency of the emitter is assumed. This is not needed in this case. In the case of continuous wave measurements, a similar PL decay lifetime is assumed. This is justified as it has been verified experimentally and theoretically to be relatively insensitive to the details of QD sizes and composition in the parameter range relevant for the investigated samples. Additionally, $\mu\text{-PL}$ setup used (see Section 3.5) is less sensitive to the differences in NW-to-NW adjustment than the setup with fiber-coupled single-photon detectors, which would have been used for photon extraction efficiency measurements. Due to their relative character, the provided results are also independent of the transmission of the experimental setup, which is another source of uncertainty in the case of evaluation of absolute photon extraction efficiency. Figure 5.4(e) presents the excitation power dependency of the integrated emission

intensity. Error bars show statistical error for 3 randomly selected nanowires from each sample. The results clearly demonstrate that the optimized NWs (red points) exhibit the highest integrated intensity at saturation, nearly one order of magnitude higher than the other samples. This outcome validates the numerical FDTD predictions and confirms the successful experimental realization of the optimized NW-QD waveguide design for enhanced photon extraction in the telecom band.

5.5 Summary and conclusions

In this chapter, the investigation of the growth of InP shell morphology of ZB NWs with InAsP QD embedded emitting in the telecom range is conducted. First, a peculiar three-segment morphology is observed, picturing a complex balance between the axial and radial growth in the NW. The growth parameters are explored, with its influence in the waveguide geometry and the tuning of the growth conditions systematically investigated. FDTD simulations guided the design of the optimal waveguide geometry, highlighting the influence of each waveguide parameter in the final extraction efficiency. The optimization of a waveguide growth protocol is achieved, with final waveguide tuned to the optimal values from the modelling. The optimized structures exhibit nearly an order of magnitude higher emission intensity compared to unoptimized designs, underlying the importance of the waveguide morphology tuning.

Chapter 6: Investigation of the wurtzite crystal phase purity in $\text{InAs}_x\text{P}_{1-x}$ NWs

Introduction

In the previous chapters, we have focused on the realization of $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP NWs grown along the $\langle 100 \rangle$ direction. This choice, which leads to the ZB crystal phase, has the important advantage of eliminating stacking faults, thereby avoiding charge traps and enhancing the structural quality of the NWs. Moreover, this growth direction and crystal phase combination has not been previously explored in the literature for $\text{InAs}_x\text{P}_{1-x}$ /InP QDs, making it a novel approach introduced in this thesis. In this chapter, however, I shift back to the more commonly investigated configuration of $\text{InAs}_x\text{P}_{1-x}$ /InP NWs grown along the $\langle 0001 \rangle$ direction, which typically results in WZ crystal phase. This system, as discussed in Chapter 2, has been extensively studied in the literature for QD growth. However, a key drawback of WZ $\langle 0001 \rangle$ NWs is their strong tendency to show stacking faults, which significantly degrades their optical properties and constraint the flexibility in the choice of QD planar dimensions¹⁴⁶. The WZ crystal phase, despite this drawback, presents some fascinating features compared to ZB. First, it is a phase peculiar of III-V NWs but absent in their bulk form⁴³. Due to the different energy bands in the WZ crystal phase, for example in AlGaAs, GaP and other III-V materials, an indirect-bandgap is predicted to become direct in the WZ crystal phase^{165,182,183}. Second, $\text{InAs}_x\text{P}_{1-x}$ NW-QDs grown along the $\langle 0001 \rangle$ direction with a WZ crystal phase are predicted to exhibit vanishing fine-structure splitting (FSS)¹²⁸. This property makes them excellent candidates as sources of entangled photon pairs, which are essential for applications requiring entangled photons¹⁸⁴ like quantum teleportation¹⁸⁵, quantum cryptography³, and particular quantum information protocols¹⁸⁶. Beyond their relevance for quantum optics, ternary $\text{InAs}_x\text{P}_{1-x}$ NWs are intrinsically interesting

structures due to their remarkable piezoelectric properties^{187,188}, low effective mass and high electron mobility¹⁸⁹. These characteristics make them attractive for the realization of high-performance electronic devices^{152,188–190}, independently of their use as photon emitters. However, also for these applications, the requirement of a strict control over the crystal phase purity of these WZ $\text{InAs}_x\text{P}_{1-x}$ NWs must be fulfilled. Extensive studies on binary InP and InAs NWs have shown that the NW crystal phase severely depends on the growth parameters such as temperature, V/III ratio, precursor fluxes, and NW diameter. The latter dependence has been linked to the Gibbs-Thomson effect¹⁰⁰, with pure WZ InP NWs being demonstrated only at very small catalyst diameters (up to 20 nm)⁹⁸, while in InAs the WZ phase is favoured at larger diameters, though still diameter-dependent¹⁰⁰. By contrast, very little is known about the stabilization of the WZ phase in the ternary $\text{InAs}_x\text{P}_{1-x}$ NWs. This chapter addresses this gap by presenting new insights into the crystal phase control of ternary $\text{InAs}_x\text{P}_{1-x}$ NWs. In particular, Section 6.1 reports the growth of NWs with different compositions and diameters, together with a systematic study of their crystal phase purity. A dependence between the NW diameter, the composition, and the WZ crystal phase purity is observed. Section 6.2 provides an energetic model, developed in collaboration with Prof. Valdimir G. Dubrovskii, to interpret the observed dependence on NW composition and diameter. Finally, section 6.3 reports a summary and the conclusions. The results presented here have been published in Ref. 18.

6.1 $\text{InAs}_x\text{P}_{1-x}$ NW growth and crystal purity investigation

As discussed in the introduction, the crystal phase purity of ternary WZ $\text{InAs}_x\text{P}_{1-x}$ NWs has not yet been systematically addressed in the literature. In contrast, the binary compounds InP and InAs have been extensively studied, and their growth conditions for

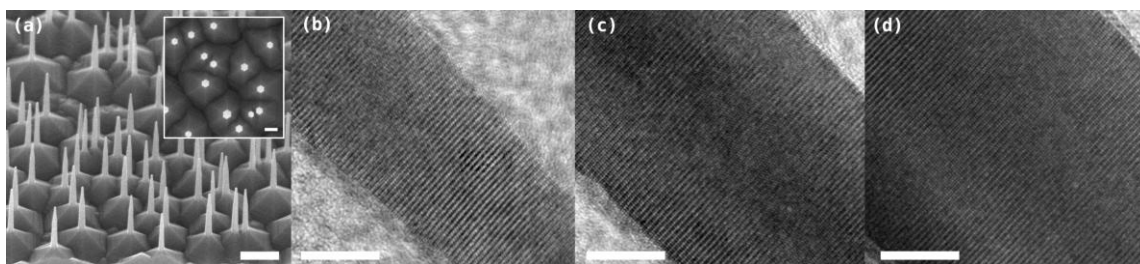


Figure 6.1.1 – (a) 45°-tilted side view SEM image of a sample of InP NWs obtained from 10 nm colloids (scale bar: 600 nm). In the inset, a topview image of the sample is provided (scale bar: 100 nm); TEM images of an exemplificative NW of the sample taken at the (b) NW tip, (c) NW center, and (d) NW base. Scale bar for all the TEM images is 10 nm.

obtaining stacking-fault-free NWs have been quite thorough. A natural strategy to tackle the problem for ternary alloy is therefore to begin from the binaries that constitute $\text{InAs}_x\text{P}_{1-x}$, i.e. InP and InAs, and then extend the investigation to the ternary system. Both binary InP and InAs are known to exhibit a pronounced diameter dependence of their crystal phase purity, with InP being the more challenging system in which to stabilize a defect-free WZ phase, as already discussed in Chapter 2. For this reason, the investigation can be initiated with InP NWs, gradually introducing arsenic to explore the evolution of the $\text{InAs}_x\text{P}_{1-x}$ crystal structure. To this aim, NWs with different diameters were grown using Au colloids of 10 nm, 20 nm, and 30 nm. The growth is performed on Fe-doped InP(111)B substrates, since the $\langle 0001 \rangle$ growth direction is the preferential orientation for stabilizing the WZ crystal phase. Defect-free WZ binary InP NWs grown from 10 nm diameter Au colloids have already been reported in the literature⁹⁶. At this diameter, the crystal phase is typically stacking fault free. Consistently, also in our experiments, pure WZ crystal structure is obtained for 10 nm colloids by properly optimizing the temperature and the fluxes. Figure 6.1.1(a) reports SEM images (side view and top view in the inset) of an InP NW ensemble grown employing 10 nm Au colloids at $(390 \pm 10)^\circ\text{C}$ for 60 minutes, with TMIn and TBP line pressures of 0.30 Torr and 0.60 Torr, respectively. The ensemble exhibits a uniform WZ crystal structure without stacking faults, as confirmed by the bright field TEM images recorded on a representative NW at the tip (panel b), center (panel c), and base (panel d). To further explore the crystal phase dependence by the diameter, NWs obtained from larger diameter colloids, specifically 20 nm and 30 nm, are then investigated.

20 nm-diameter colloid investigation

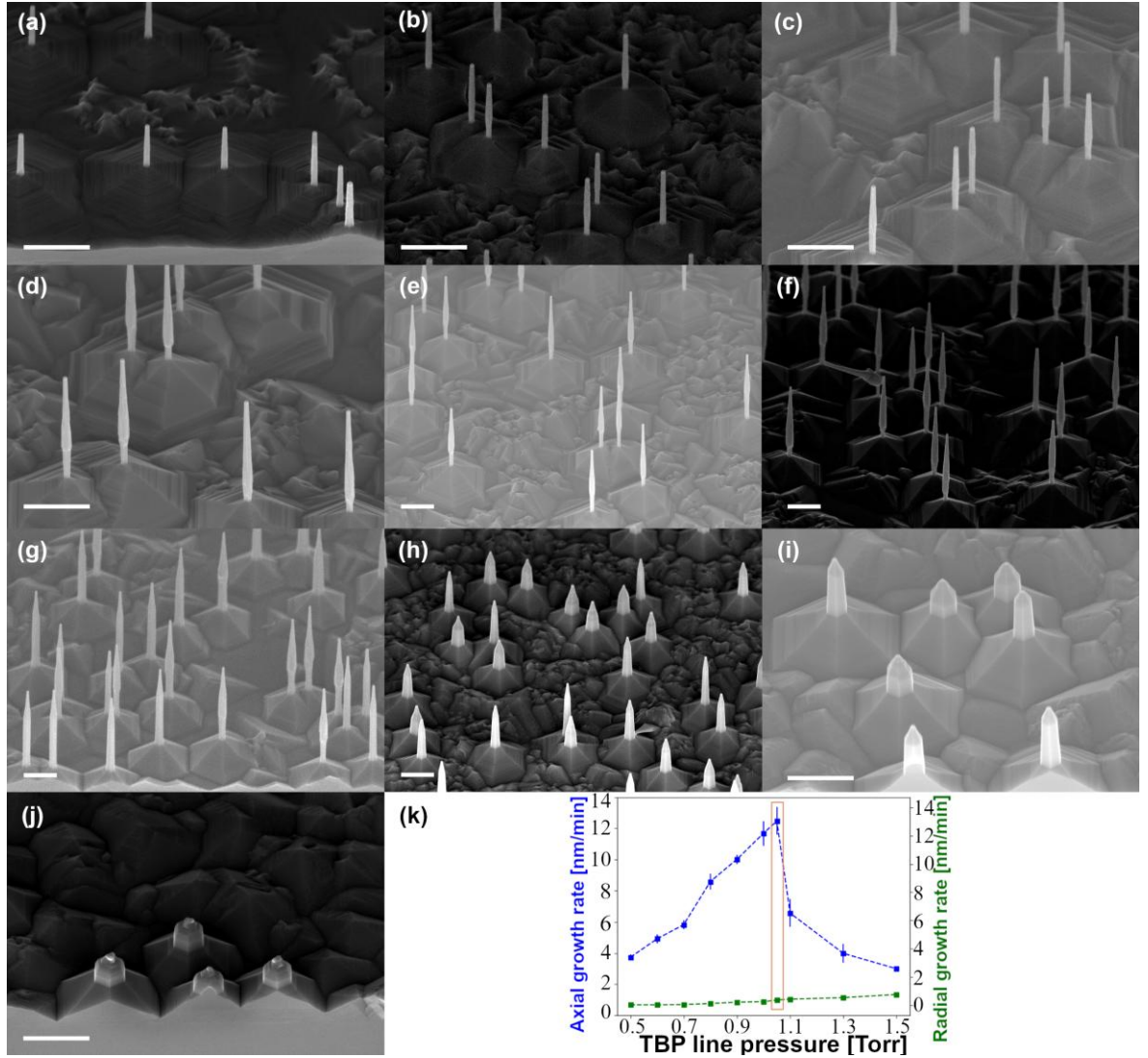


Figure 6.1.2: 45°-tilted SEM images of InP NWs grown from 20 nm-diameter colloids using TMIn = 0.30 Torr and TBP: (a) 0.50 Torr; (b) 0.60 Torr; (c) 0.70 Torr; (d) 0.80 Torr; (e) 0.90 Torr; (f) 1.00 Torr; (g) 1.05 Torr; (h) 1.10 Torr; (i) 1.30 Torr; and (j) 1.50 Torr; (k) Axial (blue) and radial (green) growth rates dependence by TBP line pressure. With an orange box, the group V line pressure chosen for the subsequent InAs_xP_{1-x} growth investigation is highlighted.

The growth of pure binary InP NWs is first investigated using 20 nm-diameter Au colloids as catalysts. All the samples are grown at $(400 \pm 5)^\circ\text{C}$ and have the same density. To identify the optimal growth conditions for binary InP, samples grown with different precursor line pressures are investigated. In particular, a series of samples is grown keeping TMIn line pressure at 0.30 Torr and varying the TBP line pressure from 0.50 Torr to 1.50 Torr, looking for the best V/III ratio. Figures 6.1.2 (a-j) show 45°-tilted SEM images of the resulting NW ensembles. The corresponding axial (blue) and radial (green) growth rates, reported in Figure 6.1.2 (k), reveal a transition from group V-limited to group III-limited growth regime, in agreement with what was observed also for ZB InP NWs in

Chapter 4. At high TBP line pressures (1.10 - 1.50 Torr), the radial growth rate exceeds the axial one, leading to strong tapering. Such conditions are not suitable when the NWs are intended to serve as a core for the subsequent QD growth. At lower TBP line pressures, NWs are untapered but local regions with enhanced radial growth are observed in some NWs in all these samples. These regions correlate with high densities of stacking faults, as previously reported in the literature⁹⁹. In our experiments, all samples grown with TBP line pressure in the range 0.50 - 0.90 Torr displayed such defective segments. However, at TBP = 1.00 Torr and 1.05 Torr, two distinct morphologies can be identified. Figure 6.1.3 (a) shows a SEM image of the sample grown employing TMIn = 0.30 Torr and TBP = 1.05 Torr, with the two NW morphologies highlighted with an orange and a green box. In particular:

- *Type 1* morphology, highlighted by the orange box, shows a characteristic bulged region with enhanced radial growth (marked by a red arrow). HRTEM measurements in Figure 6.1.3 (b) confirms that this morphology is associated with a high density of stacking faults at the buldge height.
- *Type 2* morphology, highlighted by the green box, does not exhibit such bulge. HRTEM analysis of a representative NW in panel (c) reveals a defect-free structure or, in some NWs, just few stacking faults along the NW axis (not shown here).

By comparing the two samples in which these two morphologies are evident, i.e. TBP = 1.05 Torr and TBP = 1.00 Torr, we estimate that ~42% of the NWs show the defective *type 1* morphology in the sample grown with TBP line pressure of 1.05 Torr, while a higher percentage is found in the sample with TBP line pressure of 1.00 Torr. The percentages were estimated on a total of 50 NWs per sample. Therefore, the best compromise between morphology and crystal quality is obtained for InP NWs grown at TMIn and TBP line pressures of 0.30 Torr and 1.05 Torr, respectively. This V/III ratio is subsequently chosen as the baseline for the growth of InAs_xP_{1-x} NWs. For the ternary InAs_xP_{1-x} NW growth, the total group V line pressure ($p_{\text{TBA}s} + p_{\text{TBP}}$) is then kept constant at 1.05 Torr, while varying the TBAs/TBP ratio to increase the As incorporation in the alloy. Figures 6.2.3 (d,g) show SEM images of two ensembles grown with different TBAs and TBP line pressures: 0.10 Torr and 0.95 Torr, respectively, for panel (d) and 0.20 Torr

and 0.85 Torr, respectively, for panel (g). TEM-EDS analysis is used to estimate the composition of the ternary alloy in these samples, resulting in $x = 0.09$ and $x = 0.36$, respectively. The $\text{InAs}_{0.09}\text{P}_{0.91}$ sample still shows stacking faults, as illustrated in the TEM and HRTEM images of Figure 6.1.3 (e,f). In contrast, $\text{InAs}_{0.36}\text{P}_{0.64}$ ensemble is defect-free WZ crystal phase in all the measured NWs, as confirmed by the TEM and HRTEM images of representative NW in Figures 6.1.3 (h,i). These results, interestingly, show that the sample with higher As content drives a transition from polytypic to pure WZ crystal

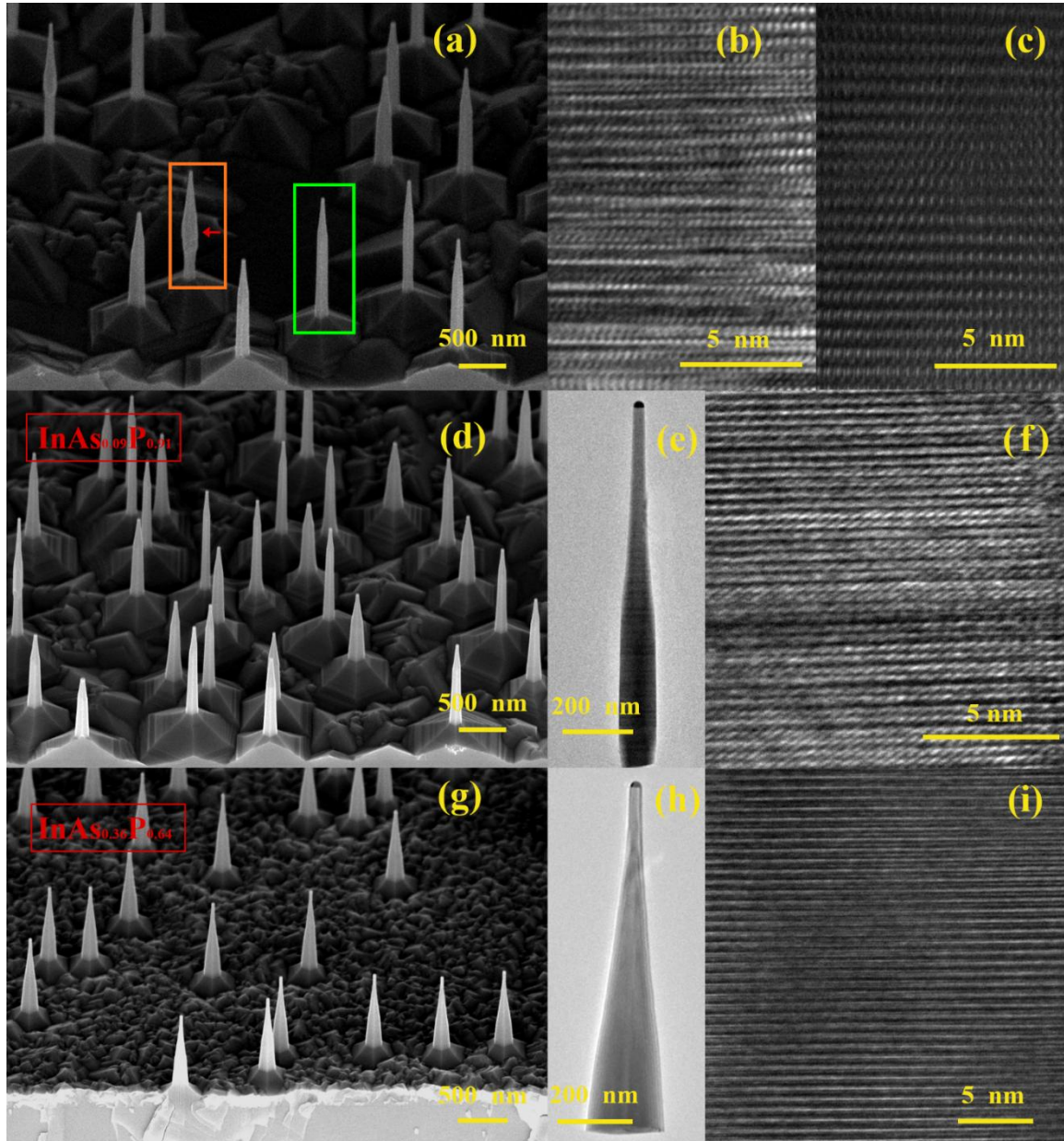


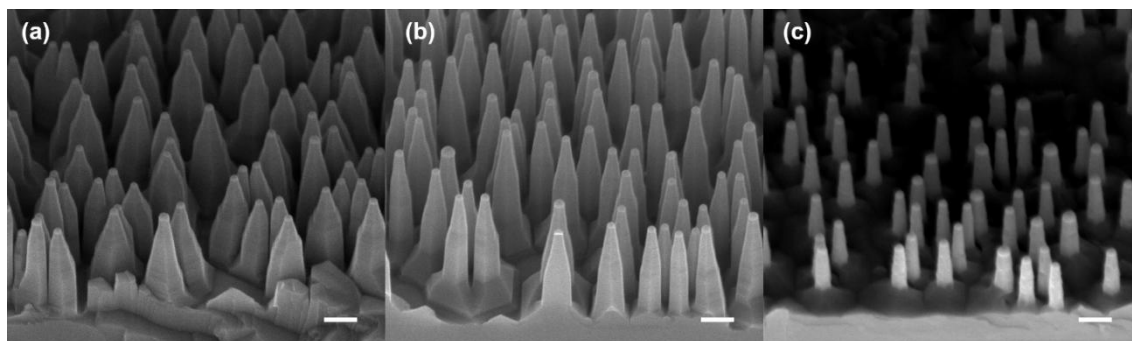
Figure 6.1.3 – (a) 45°-tilted side view SEM image of pure InP NWs grown from 20 nm Au nanoparticles. Orange and green boxes highlighted type 1 and 2 morphology, respectively. HRTEM images of these two morphologies are reported in panel (b) and (c), respectively; (d) SEM image of $\text{InAs}_{0.09}\text{P}_{0.91}$ ensemble and a TEM (panel e) and HRTEM (panel f) of a representative NW with stacking faults; (g) 45°-tilted side view SEM image of $\text{InAs}_{0.36}\text{P}_{0.64}$ NW ensemble with defect free structure, as demonstrated by the TEM (panel h) and HRTEM (panel i) of a representative NW.

structure in NWs grown from 20 nm colloids. By comparing panels (d) and (g) it is also evident that higher As incorporation leads also to an increased radial growth, resulting in more tapered NWs grown at the same temperature. This is likely due to the higher sticking coefficient of As compared to P, which enhances the nucleation probability on the NW sidewalls. In addition, the average axial growth rate decreases monotonically with increasing As content in the alloy, from ~ 13 nm/min in pure InP to ~ 9 nm/min in $\text{InAs}_{0.36}\text{P}_{0.64}$.

30 nm-diameter colloid investigation

A similar study is performed on larger diameter NWs obtained from 30 nm-diameter Au colloids. As in the previous case, the investigation starts with binary InP NWs to determine suitable baseline growth conditions for the ternary alloy. Figure 6.1.4 shows SEM images of InP NW ensemble grown at $(400 \pm 5)^\circ\text{C}$ with TMIn line pressure of 0.3 Torr and TBP line pressure of 1.05 Torr (panel a), – i.e. similar to the best line pressure for 20 nm colloids discussed above –, TBP = 0.90 Torr (panel b) and TBP = 0.40 Torr (panel c). All samples exhibit NWs longer than 300 nm and with comparable densities. Unlike the 20 nm case, no distinct *type 1* and *type 2* morphologies are observed in these samples. However, high TBP line pressures strongly enhanced radial growth. For all investigated V/III ratios, the NWs exhibited WZ crystal phase with a high density of stacking faults. Thus, the sample grown at TBP = 0.40 Torr is selected as the starting point for alloy studies, since it produced almost untapered NWs with limited radial growth. Figure 6.1.5(a) shows another 45° -tilted SEM image of such a sample, with TEM and HRTEM of a representative NW in panels (b) and (c), respectively. Here, alternating

Figure 6.1.4: 45° -tilted SEM images of InP NWs grown with 30 nm Au colloids using TMIn line pressure at 0.30 Torr and TBP at: (a) 1.05 Torr; (b) 0.90 Torr; and (c) 0.40 Torr. Scale bars are 200 nm in all the images.



WZ and ZB segments within a polytypic structure can be observed, consistent with earlier reports on increased defect densities in larger-diameter InP NWs⁹⁹. Alloy growth is then investigated under the same TMIn line pressure of 0.30 Torr and keeping the total group V line pressure ($p_{\text{TBA}s} + p_{\text{TBP}}$) at 0.40 Torr. Figure 6.1.5(d) shows an SEM image of an $\text{InAs}_{0.46}\text{P}_{0.54}$ ensemble grown with TBP and TBAs line pressures of 0.25 Torr and 0.15 Torr, respectively. TEM and HRTEM analysis of a representative NW in panels (e) and

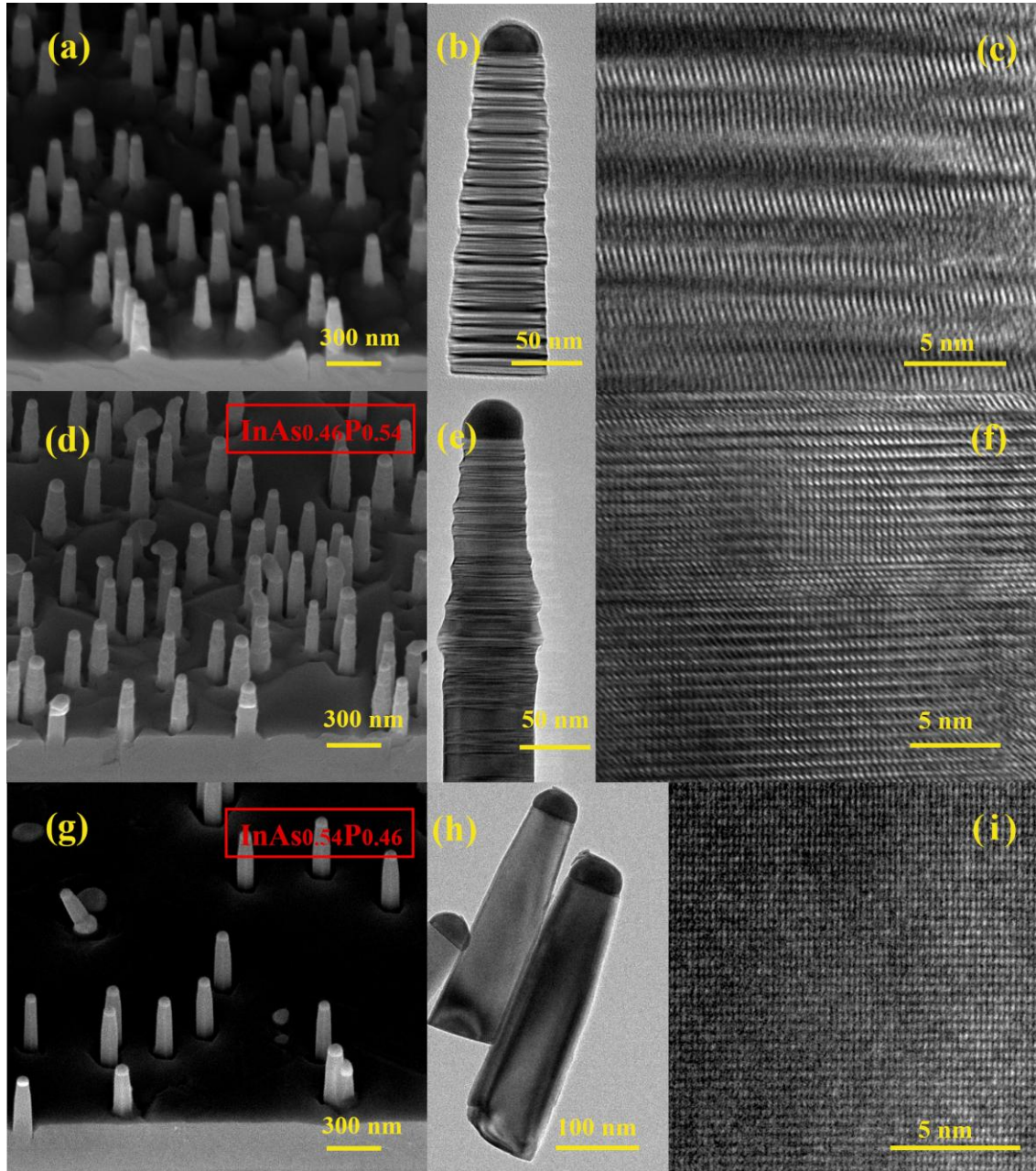


Figure 6.1.5: (a) 45°-tilted SEM image of InP NWs grown from 30 nm Au diameter colloids with TMIn and TBP line pressures of 0.30 Torr and 0.40 Torr, respectively. (b) a TEM image of a representative NW and its HRTEM image in panel (c); (d) 45°-tilted side view SEM image of $\text{InAs}_{0.46}\text{P}_{0.54}$ NWs, with the corresponding TEM image in panel (e) and HRTEM image in panel (f); (g) 45°-tilted side view SEM image of $\text{InAs}_{0.54}\text{P}_{0.46}$ NWs that exhibit pure WZ crystal phase, as demonstrated by the corresponding TEM (h) and HRTEM (i) images.

(f) reveal the presence of stacking faults throughout the NWs of this sample. Defect free WZ NWs are obtained by further adding As content in the alloy. Figure 6.1.5 (g) presents an SEM image of $\text{InAs}_{0.54}\text{P}_{0.46}$ NWs grown with TBAs and TBP line pressures both at 0.20 Torr. TEM and HRTEM analysis (panels h,i) confirm a pure WZ crystal phase. All measured NWs (at least 20) displayed the same defect-free structure. It is worth noting that increasing the As content also reduced the vertical yield of the NWs; a significant fraction of the NWs failed to nucleate, as evidenced by the presence of catalyst NPs on the substrate in Figure 6.1.5(g). This is likely related to the difficult nucleation of NWs on the substrate surface under the growth conditions that were chosen to obtain untapered NWs in pure WZ phase, rather than maximize their yield. Interestingly, no significant changes in axial or radial growth rates can be observed between $\text{InAs}_{0.46}\text{P}_{0.54}$ and $\text{InAs}_{0.54}\text{P}_{0.46}$. This suggests that, contrary to earlier hypotheses⁹⁹, reduced axial growth rates alone are not sufficient to guarantee pure WZ phase in III-V NWs, at least in our case of ternary $\text{InAs}_x\text{P}_{1-x}$ NWs.

From this systematic study, it is clear that the NW crystal phase depends strongly on composition. A critical As composition x_c can be defined, above which the structure transits from polytypic WZ/ZB to pure WZ. This threshold is diameter-dependent, yielding $x_c = 0.46$ for NWs grown with 20 nm-diameter colloids, and $x_c = 0.54$ for NWs obtained with 30 nm-diameter colloids. It has been discussed in literature that defect formation in both InP and InAs binary NWs could be related to the In concentration in the liquid catalyst droplet during the NWs growth^{96,100}. Therefore, to further investigate the origin of defect formation, TEM-EDS measurements of the catalyst composition and the droplet contact angles are measured for all the samples discussed above. As already mentioned in Chapter 3, it has been demonstrated on binary NWs that cooling down the samples after the growth in absence of group V fluxes doesn't alter significantly the catalyst composition during the growth^{113,160}. Although in situ measurements during the growth would be more accurate, we cooled down all the samples in this similar way in order to have an estimation of the catalyst composition during the growth and a comparison between the different samples. Table 6.1 provides the results of such measurements done on at least 20 NWs for each sample, with the average values and the standard deviations reported in the table. These data show that the In/Au ratio inside the catalyst change between 20 and 30 nm diameter samples but, however, no significant

change is observed in the nanoparticle (NP) composition between binary InP and ternary InAs_xP_{1-x} NWs. So, unlike the case of binary InP NWs, the crystal phase purity of ternary InAs_xP_{1-x} alloy seems not directly linked to the In content in the catalyst NPs. Of course, both P and As are typically not detected in the NPs due to their high volatility, thus nothing can be said about these element content. In addition, the average contact angle remained constant at $\sim 95^\circ$ in all the samples, independent of composition.

NP diameter (nm)	As fraction x	In (at%)	Au (at%)	Average contact angle (deg)
20	0.00	54 $\pm$ 2	46 $\pm$ 2	94 $\pm$ 5
20	0.09	52 $\pm$ 8	48 $\pm$ 8	87 $\pm$ 5
20	0.36	49 $\pm$ 3	51 $\pm$ 3	93 $\pm$ 3
30	0.00	65 $\pm$ 2	35 $\pm$ 2	84 $\pm$ 8
30	0.46	68.6 $\pm$ 0.9	31.4 $\pm$ 0.9	100 $\pm$ 5
30	0.54	65.3 $\pm$ 0.8	34.7 $\pm$ 0.8	98 $\pm$ 3

Table 6.1: In and Au percentages and contact angles of the NPs on top of different InAs_xP_{1-x} NWs, measured with EDS-TEM and TEM.

6.2 Modelling of the crystal phase dependence by the NW composition and diameter

To understand the dependence of the NW crystal structure on composition and diameter for ternary alloy, a simple model is developed to rationalize the experimentally observed trends. The model is based on energetic considerations and extends the well-established binary NW models to the ternary alloy case. As a first approximation, the vapor-solid growth of tapered shells around the NW core is neglected, assuming that the crystal phase is entirely determined by the VLS growth step of the core. This assumption is justified in binary III-V NWs, since it has been experimentally observed that tapered shells inherit the crystal phase of their VLS-grown cores^{61,71,191,192}. According to Refs. ^{191–196}, the condition for the formation of VLS NWs in the WZ phase corresponds to the preferential

stabilization of vertical WZ facets with respect to truncated ZB facets. This can be expressed by the following inequation:

$$\Delta\gamma = \frac{\gamma_\phi}{\cos\phi} - \gamma_p \tan\phi - \gamma_s + \gamma_L \sin\beta > 0 \quad (6.1)$$

Where:

- β is the droplet contact angle,
- ϕ is the angle of the truncated facet with respect to the vertical,
- γ_ϕ is the solid-liquid surface energy of the truncated facet,
- γ_p is the solid-liquid surface energy of horizontal facet under the droplet,
- γ_s is the solid-vapor surface energy of vertical WZ facet,
- γ_L is the liquid-vapour surface energy of of the droplet.

A schematic of the ZB and WZ configurations and the relevant parameters in Equation (6.1) are shown in Figure 6.2 (a). The two solid-liquid surface energies, γ_ϕ and γ_p , are phase independent^{43,61}. Furthermore, surface energies γ are generally assumed to be radius-independent for sufficiently thick NWs, where the edge contributions are negligible^{43,191–196}. However, for thin NWs, these edges separating the side facets become important contributors to the total formation energy of the hexahedral NWs^{61,197–199}. The liquid surface energy γ_L and the planar horizontal facet energy γ_p under the droplet, have

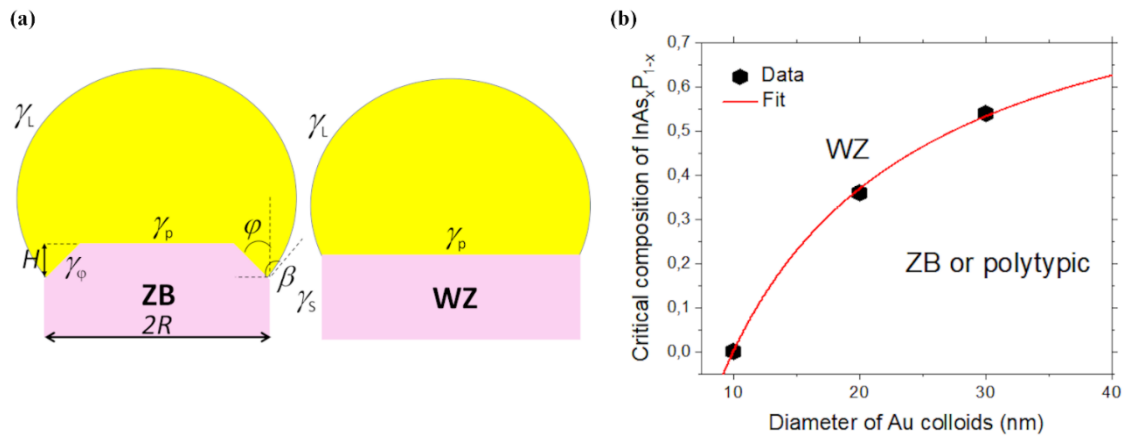


Figure 6.2: (a) Illustration of the truncated ZB and planar WZ growth interfaces under the catalyst droplet, showing the surface energies of interest; (b) Critical composition of $\text{InAs}_x\text{P}_{1-x}$ NWs x_c versus the Au nanoparticle diameter (symbols), fitted by Equation (5.6) at $x_c^\infty = 0.96$, $A = 5$ nm and $B = 3$ nm (red line).

no edges and are hence independent of the NW top radius (which is directly related to the nominal radius of Au colloids R). In contrast, the radius dependence enters in the terms γ_ϕ and γ_s . In fact, six equivalent facets of truncated ZB NWs and vertical WZ NWs are separated by edges. The surface energies γ per surface area are $\sim RH$, with H being the truncation height depicted in Figure 6.2 (a). Hence, the edge energies are inversely proportional to R . The total surface energies with the edge contributions, i.e. the radius dependence, are given by Refs.^{61,198}:

$$\begin{cases} \gamma_\phi = \Gamma_\phi + \frac{\epsilon_\phi}{R} \\ \gamma_s = \Gamma_s + \frac{\epsilon_s}{R} \end{cases} \quad (6.2)$$

Here, Γ denotes the surface energy of flat facets and ϵ is the specific edge energy per unit length, with $\gamma_\phi \rightarrow \Gamma_\phi$ at large R . For $\text{InAs}_x\text{P}_{1-x}$ ternary NWs, the solid-vapor and liquid-vapor surface and edge energies depend also on the alloy composition x . These energies for III-V ternary NWs in both ZB and WZ phases are unknown. Therefore, the simplest linear dependence on the composition can be used in the first approximation^{200,201}:

$$\begin{cases} \Gamma_\phi = \Gamma_\phi^0(1 - c_\phi^\Gamma \cdot x), & \epsilon_\phi = \epsilon_\phi^0(1 - c_\phi^\epsilon \cdot x) \\ \Gamma_s = \Gamma_s^0(1 - c_s^\Gamma \cdot x), & \epsilon_s = \epsilon_s^0(1 - c_s^\epsilon \cdot x) \\ \gamma_p = \gamma_p^0(1 - c_p \cdot x) \end{cases} \quad (6.3)$$

Here, the surface and edge energies labelled “0” correspond to pure InP NWs, and x -independent coefficients c describe linear interpolation of the surface and edge energies between pure InP and InAs. According to the calculations of Ref. 202, the vapor-solid surface energy Γ_s^0 of unpassivated vertical WZ facets $(1\bar{1}00)$ and $(11\bar{2}0)$ at zero temperature are 23.5% lower for InAs NWs, corresponding to a positive $c_s^\Gamma = 0.235$. This corresponds to the well-known trend of having stable WZ phase in binary InAs NWs, where the ZB stacking is the exception rather than the rule^{61,193}. In contrast, nothing is known about the edge energies of ternary NWs and the solid-liquid surface energies Γ_ϕ and γ_p , which leads to the fact that the other coefficients c in Equations (6.3) can be of either signs. The surface energy of liquid droplet should be independent of negligibly small concentrations of P and As atoms and even on the Au concentration, because the

lower surface energy liquid In accumulates at the droplet surface^{193–195}. The droplet contact angle β is the only kinetic parameter entering Equation (6.1). It generally depends on the total V/III ratio and As/P flux ration (and hence the composition x) due to kinetic growth effects¹¹³. Even though a careful study with in-situ TEM could provide interesting and more precise insights about this parameter, we can use as a first approximation a linear interpolation of $\sin\beta$ in Equation (6.1) of the form:

$$\sin\beta(x) \simeq \sin\beta_0 + (\cos\beta_0)c_\beta \cdot x \quad (6.4)$$

With a coefficient c_β , and β_0 as the average contact angle of the droplets on top of pure InP NWs. This interpolation assumes a small variation of the contact angle compared to β_0 , which is the contact angle for pure InP NWs. Post-growth measurements reported in Table 6.1 show that the average contact angle of all the NWs is only slightly above 90° . In this case, the composition dependence of the contact angle is very weak, but this is not critical for this semi-quantitative model. Using Equations (6.2), (6.3) and (6.4) in Equation (6.1), the condition of the preferred WZ phase formation is obtained in the form $\Delta\gamma(R, x) \geq 0$. This allows to find the critical composition x_c corresponding to the ZB-to-WZ phase transition as a function of the radius R . By manipulating Equation (6.1) with the terms introduced by Equations (6.2), (6.3) and (6.4), the condition for WZ stability hence becomes:

$$\Delta\gamma_0 - \frac{a}{R} + \left(d + \frac{b}{R}\right) \cdot x > 0 \quad (6.5)$$

This inequation contains three terms:

- $\Delta\gamma_0 = \frac{\Gamma_\phi^0}{\cos\phi} - \gamma_p^0 \tan\phi - \Gamma_s^0 + \gamma_L \sin\beta_0$, being the surface energy difference that determines the crystal phase of thick InP NWs at a contact angle of the catalyst droplet β_0 .
- a/R being the composition-independent edge contribution, with $a = \epsilon_s^0 - \frac{\epsilon_\phi^0}{\cos\phi}$

- The third term is x -dependent part of the inequation and contains two contributions: from the surface $d = \Gamma_s^0 c_s^\Gamma + \gamma_p^0 c_p \tan\phi + \gamma_L(\cos\beta_0)c_\beta - \frac{\Gamma_\phi^0 c_\phi^\Gamma}{\cos\phi}$, and from the edge energies (b/r), with $b = \epsilon_s^0 c_s^\epsilon - \frac{\epsilon_\phi^0 c_\phi^\epsilon}{\cos\phi}$

The WZ phase is thus energetically favoured when:

$$x > x_c = x_c^\infty \frac{R - A}{R + B} \quad (6.6)$$

With $x_c^\infty = -\frac{\Delta\gamma_0}{d}$, $A = \frac{a}{\Delta\gamma_0}$ and $B = \frac{b}{d}$. The parameters x_c^∞ , A and B lumps together the largely unknown energetic factors influencing the crystal phase trend in thin III-V ternary NWs, and yield simple analytic shape of the critical curve and $x_c(R)$. For x below the critical curve $x_c(R)$, the crystal phase can be polytypic rather than pure ZB due to a periodically changing geometry of the growth interface^{192,195}.

This model describes different crystal phase trends depending on the signs and magnitudes of the coefficients entering Equation (6.6). Figure 6.2 (b) shows with the black spots the data of $x_c(R)$ dependence on the catalyst radius experimentally observed. These data demonstrate that pure WZ phase of $\text{InAs}_x\text{P}_{1-x}$ grown in the experiments requires higher fractions of As for larger radii. The first data point in Figure 6.2 (b) corresponds to pure WZ crystal phase obtained in InP NWs at $R = 5 \text{ nm}$, which fix $A = 5 \text{ nm}$ in Equation (6.6). Monotonically increasing dependence $x_c(R)$ in the investigated range of NW compositions and Au radii requires positive x_c^∞ and positive A . From the expression of A , this condition corresponds to differently signed coefficients $\Delta\gamma_0$ and d , and equally signed coefficients $\Delta\gamma_0$ and a (i.e. $\Delta\gamma_0 > 0$, $a > 0$ and $d < 0$, or $\Delta\gamma_0 < 0$, $a < 0$ and $d > 0$). The sign of B in Equation (6.6) is less important. For example, the data points can reasonably be fitted also by $x_c = x_c^\infty(1 - A/R)$ at $B \cong 0$. The fit shown in Figure 6.2 (b) is obtained with $x_c^\infty = 0.96$, $A = 5 \text{ nm}$ and $B = 3 \text{ nm}$. This corresponds to pure WZ phase of very thin InP NWs ($R \leq 5 \text{ nm}$), ZB or polytypic phase of thicker binary InP NWs and almost pure WZ phase for thicker InAs NWs under the explored growth conditions. The trend of a more stable WZ phase of InAs NWs relative

to InP and all other binary III-V NWs is well-known and has been reproduced by different epitaxy techniques^{61,104}.

6.3 Summary and Conclusions

In this chapter, the crystal phase purity of III-V ternary alloy $\text{InAs}_x\text{P}_{1-x}$ NWs grown along the $\langle 0001 \rangle$ direction has been investigated. While binary InP NWs are known to exhibit an increasing density of defects with diameter, our results confirm this trend and demonstrate that the incorporation of As into the alloy can overcome this limitation. Specifically, the addition of As stabilizes the WZ crystal phase by suppressing stacking faults, provided that the alloy composition exceeds a critical value x_c . Importantly, this critical composition x_c is radius-dependent. A simple energetic model has been developed to explain these findings. In this framework, the radius dependence arises from edge contributions into the overall energy balance, whereas the composition dependence is introduced via the variation of effective surface energies with alloy composition. Although further refinements could be achieved by including kinetic contributions and by exploring a broader range of NW diameters and compositions, the model successfully reproduces the experimental data. The results presented here suggest a pathway to improve crystal phase purity in InP-based NW-QDs emitters presented in the framework of this thesis. In fact, by replacing the InP matrix with an $\text{InAs}_x\text{P}_{1-x}$ alloy of sufficiently high As content, it is possible to obtain pure WZ NWs, thereby enabling the realization of high-quality single-photon sources along the $\langle 0001 \rangle$ direction. This approach is particularly relevant for applications requiring vanishing fine-structure splitting for the generation of entangled photon pairs. Finally, the methodology developed in this chapter can be extended to other III-V ternary NW systems and different epitaxial techniques.

Chapter 7: Conclusions and outlook

A crucial milestone of this thesis is the growth and optimization of ZB $\text{InAs}_x\text{P}_{1-x}$ QDs embedded in InP nanowires (NW-QDs) emitting in the telecommunication bands, addressing the main challenges in the state of the art and proposing alternative routes to outcome them. The NW-QDs have been grown by chemical beam epitaxy (CBE), while structural, chemical, and optical properties were investigated through electron microscopy and micro-photoluminescence measurements.

The first part of this work tackled the challenges in achieving emission in the telecom range by investigating the growth of ZB NWs along the $\langle 100 \rangle$ crystallographic direction. This approach allows for a relaxation for the catalyst diameter constraint typically imposed to avoid crystal defects in the conventional $\langle 0001 \rangle$ -oriented NWs. As a result, emission in the telecom range can be achieved without the need for very high aspect ratios, which are associated with a dramatic decrease in brightness. For the first time, a reproducible growth protocol enabling the fabrication of $\text{InAs}_x\text{P}_{1-x}/\text{InP}$ heterostructure NWs with pure ZB phase along the $\langle 100 \rangle$ direction has been successfully established, with the main growth challenges identified and discussed. In particular, a strong dependence of the heterostructure straight growth on the temperature at which growth interruptions are performed has been observed. Moreover, a distinct behaviour between $\text{InP}/\text{InAs}_x\text{P}_{1-x}$ and InP/InAs heterostructures was found, with the latter requiring a higher indium content inside the catalyst droplet to achieve straight growth. The systematic study of the QD feature enabled the tuning of the emission wavelength across the telecom bands, reaching up to the third telecom window.

In the second part, the optimization of the NW morphology for the realization of an efficient photonic waveguide was successfully achieved. The investigation revealed a

complex growth dynamics in ZB NWs, mainly attributed to the different surface facets and their polarity, which govern the balance between axial and radial growth and result in a characteristic three-segment morphology. Theoretical modelling was performed to identify the most relevant parameters for light guiding and adiabatic funnelling of the electromagnetic field along the NW axis, aiming to maximize photon extraction efficiency. The most critical growth parameter was found to be the total TMIn precursor flux, with a double-step InP shell growth approach allowing tuning of the key geometrical quantities predicted by the calculations. The optimized waveguide geometry led to an experimental enhancement of the QD emission intensity by one order of magnitude compared to non-optimized structures.

The results of this thesis establish $\text{InAs}_x\text{P}_{1-x}$ QDs in ZB InP NWs grown along the $\langle 100 \rangle$ direction as a promising platform for quantum photonics applications. This approach offers several advantages, including relaxed constraints related to crystal defects, reduced substrate processing, and great flexibility in the control of QD planar dimensions. Nevertheless, some challenges remain. The single-photon purity of these emitters still needs to be demonstrated through second-order autocorrelation measurements, which now can be reached thanks to the signal level achieved in this work. Furthermore, the observed spectral diffusion – although not caused by stacking faults, since the investigated NW-QDs are fully stacking-fault free – should be addressed both experimentally and theoretically. Possible strategies include improving the abruptness of the QD interfaces with a double GI and reducing the background contamination in the growth chamber. The investigation of smaller-diameter NWs (~ 35 nm) grown from 20 nm catalyst nanoparticles also revealed a narrowing of the emission linewidth (not shown in this thesis), suggesting that the QDs presented in this thesis may exhibit a lateral confinement comparable to QD dashes, with non-negligible effects on their quantum confinement regime. Despite these open questions, the results presented here clearly demonstrate that ZB $\text{InAs}_x\text{P}_{1-x}$ NW-QDs represent a viable and scalable platform for telecom-wavelength quantum light sources, combining low emitter density, strong emission intensity, and the intrinsic advantage of direct waveguide integration without the need for pre- or post-growth nanofabrication. Future perspectives may exploit this platform and its intrinsic axial stacking capabilities for the realization of coupled QD

systems, potentially enabling lambda-like electronic energy levels essential for advanced quantum communication schemes.

In parallel, this thesis has also explored an alternative route to address the issue of diameter-dependent stacking fault formation in wurtzite (WZ) InP/InAs_xP_{1-x} NWs grown along the <0001> direction. Remarkably, it has been shown that pure WZ crystal phase can be achieved by appropriately tuning the arsenic content in the ternary alloy composition at relevant diameters for quantum confinement. The insights gained in this work have been supported by the development of a first theoretical model explaining this phenomenon on energetic grounds. Low-As-content InAs_xP_{1-x} NWs can thus serve as a high-quality matrix for embedding higher-As-content QDs, eliminating stacking faults even for larger catalyst diameters. This finding makes the conventional WZ <0001> NW platform more versatile and particularly attractive for applications requiring vanishing fine-structure splitting for entangled-photon pair generation.

Appendix A1: Tunable GaAs_xP_{1-x} QD emission in WZ GaP NWs

Introduction

This appendix provides a summary of the work conducted as a side project during the PhD activity. The study focuses on the realization of GaAs_xP_{1-x} QDs embedded in GaP NWs grown along the <0001> direction with a WZ crystal structure. The choice of this material system is motivated by the properties of GaP, which exhibits a high transparency range (0.6 - 1.1 μm)¹⁸³ and a theoretically predicted quasi-direct bandgap peculiar of the WZ phase, with values between 2.18 - 2.25 eV^{84,182,183}. These characteristics make GaP a highly promising candidate for the realization and on-chip integration of single-photon sources. In particular, the large lattice-mismatch between GaAs and GaP of 3.7% and the transformation of the bandgap from indirect (in bulk GaP) to quasi-direct (in WZ NWs) make these NW-QDs particularly appealing for fundamental and applied investigations. Previous works in literature have explored the growth of GaAs/GaP NW-QDs primarily in the ZB crystal phase. Intense PL has been reported from ZB GaAs QDs embedded in GaAs_xP_{1-x} NWs, showing antibunching up to 160 K, a full width at half-maximum (FWHM) of 1.2 meV, and an emission energy centered at 760 nm. It has also been demonstrated that GaAsP insertions can be incorporated into a single ZB GaP NW and different QD emission energy by varying the As content can be obtained¹²⁶. In the WZ crystal structure, the emission efficiency is expected to be higher due to the direct band gap¹⁸². Importantly, defect-free WZ GaP NWs²⁰³ and fully WZ GaAs/GaP superlattice NWs²⁰⁴ have been successfully realized via Au-assisted CBE, and control of the As/P flux ratio during the growth can allow for a high degree of tunability of the QD composition and hence light emission properties¹⁸².

In this chapter, the growth study of GaAs_xP_{1-x}/GaP NW-QDs is presented and discussed. Section A1.1 provides insights into the growth procedure and structural characterization of the dots. Section A1.2 summarizes the main result of their optical characterization.

The optical studies are carried out in collaboration with the group of Prof. De Luca at the University of *La Sapienza* (Rome, Italy). The findings of this investigation have been published in Ref.19 .

A1.1 Growth optimization of GaAs_xP_{1-x} QDs in WZ GaP NWs

The GaAs_xP_{1-x} NW-QDs are synthesized by Au-assisted VLS growth in the CBE chamber. The Au catalyst nanoparticles are prepared using two different approaches: (i) by employing colloidal Au nanoparticles with a nominal diameter of 20 nm and (ii) by in situ dewetting of a 0.02 nm-thick Au film thermally evaporated on the substrate prior to the growth. The dewetting process is performed inside the growth chamber prior to the NW-QD growth at (500 ± 10) °C under 1 Torr of TBAs line pressure, resulting in an ensemble of nanoparticles with an average diameter of (34 ± 8) nm. The resulting NW-QDs growth protocol and a schematic representation of the heterostructure are shown in Figure A1.1. The optimized growth sequence is described as follows:

- (a) Due to the large lattice-mismatch between GaAs and GaP, direct GaP NWs growth on a GaAs(111)B is not straightforward, often leading to NWs kinking or even absence of NW nucleation. To overcome this issue and exploit the planar strain relaxation of the NW geometry, a (370 ± 60) nm-long GaAs segment is first grown prior to the GaP NW growth. This segment is grown for 30 min at (500 ± 10) °C, employing Triethylgallium (TEGa) and TBAs precursor line pressures both set to 0.70 Torr.
- (b) A temperature ramp to (560 ± 10) °C is then performed in 5 minutes to reach the optimal temperature for GaP growth, as it will be discussed later. During this ramp, TEGa and TBP line pressures are gradually adjusted to their optimal values for the subsequent GaP segment growth.
- (c) A GaP segment is then grown on top of GaAs for 20 minutes, yielding an average length of (900 ± 100) nm.
- (d) A growth interruptions (GI) of 1 minute is then introduced to stabilize TBAs and TBP line pressures prior to the GaAs_xP_{1-x} QD growth.

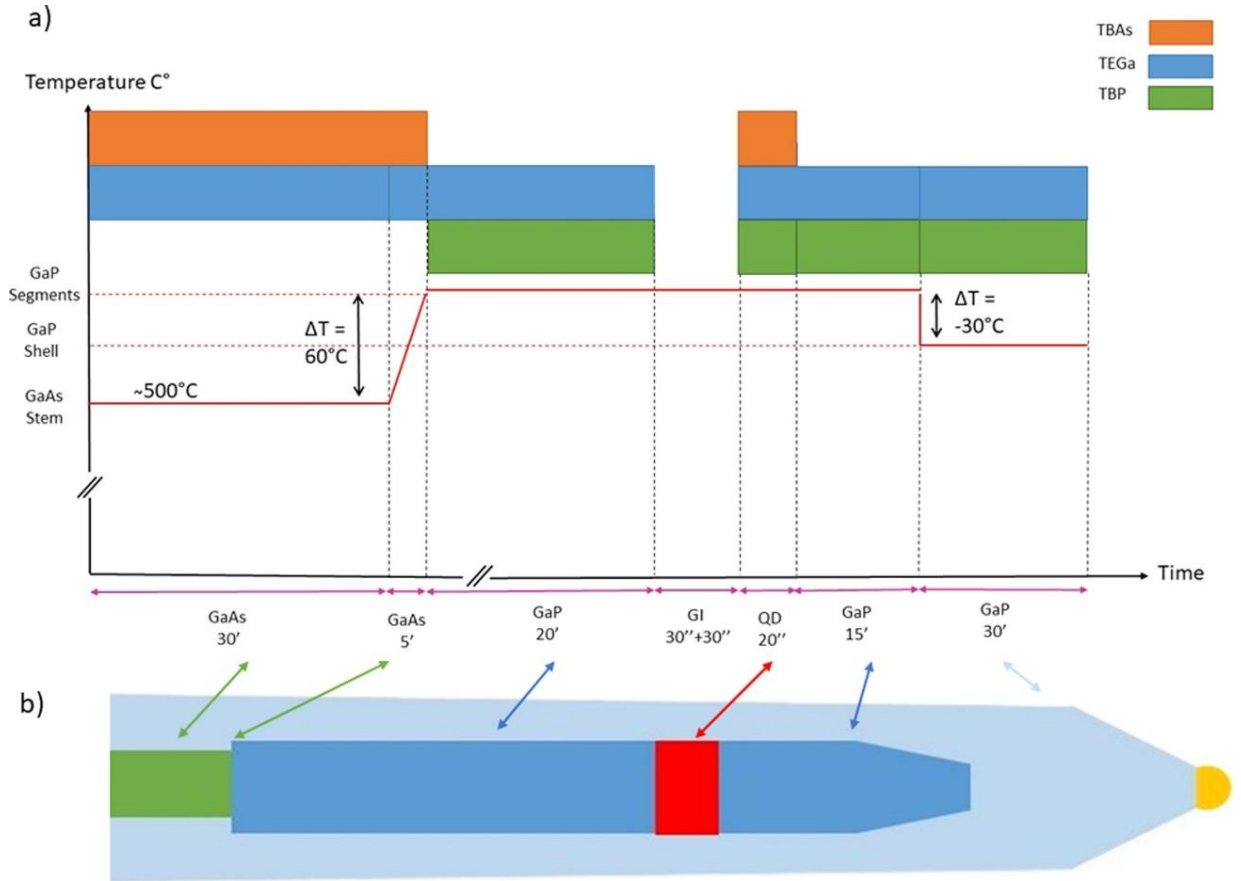


Figure A1.1: (a) Graphical representation (not in scale) of the growth procedure, with the MO precursors used for each step indicated in different colors. The GI before the QD growth is used to prepare different Group V precursor pressures to tune the QD composition. (b) Schematics (not in scale) of the resulting nanostructure at the end of the entire growth process.

- (e) The $\text{GaAs}_x\text{P}_{1-x}$ QD is subsequently grown, varying the As content in different samples in order to investigate the emission tunability as a function of composition.
- (f) Finally, a GaP tip is grown under the same temperature and precursor fluxes used for the previous GaP segment. The total NW length ranges between 1.5 μm and 2.5 μm , depending on the duration of the final GaP growth step.

Overall, the growth process required a systematic optimization of two main steps: (i) the initial GaAs+GaP segments growth conditions; and (ii) the calibration of the ternary alloy composition for QD formation. These optimizations studies are discussed in the following subsections.

A1.1.1 GaAs/GaP heterostructure optimization

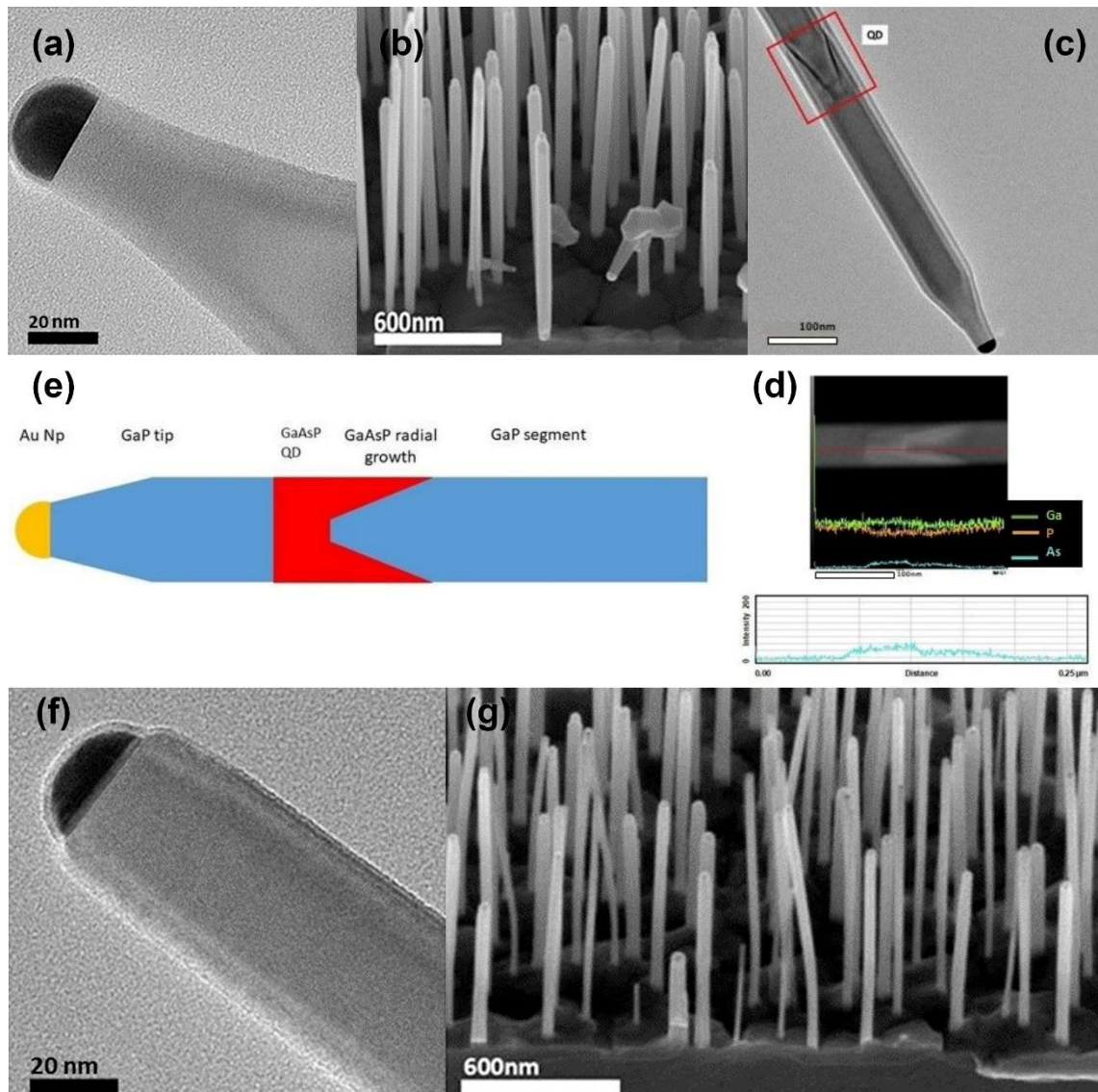
The first optimization step focuses on the interface between the short GaAs NW and the initial GaP segment grown prior to the QD. The study is carried out on samples obtained from the dewetting of a thin Au film resulting, as already mentioned, in an average diameter of (34 ± 8) nm. As reported in literature²⁰³, the growth of pure WZ GaP NWs without stacking faults requires high TBP line pressures. In these experiments, GaP NWs grown using TEGa and TBP line pressures of 0.70 Torr and 2.50 Torr, respectively, exhibited nearly perfect WZ crystal phase. However, these NWs displayed a pencil-shaped tip morphology, as shown in Figures A1.1.1 (a,b), which report a TEM image of a GaP NW tip grown with these conditions and a 45°-tilted view SEM image. The presence of a pencil-shaped GaP tip is detrimental for achieving optimal quantum confinement in the subsequent QD growth. Indeed, when GaAsP QD is grown on top of such a tip, the resulting QD assumes a non-ideal morphology. Figure A1.1.1 (c) shows a bright-field TEM image of a representative GaAsP QD (highlighted with a red box) and the corresponding STEM-EDX analysis in panel (d) confirm the non-ideal QD shape, schematized in panel (e). The data reveal the formation of a GaAsP QD with GaAsP tails radially grown around the pencil-shaped GaP tip, effectively creating a quantum well-like region beneath the QD and thus compromising carrier confinement. To overcome this issue, the GaP growth conditions are optimized to suppress the formation of the pencil-shaped tip morphology while preserving the WZ crystal phase purity of GaP. The pencil-shape morphology is likely related to parasitic vapor-solid growth on the NW sidewalls and to the intrinsically short diffusion length of Ga adatoms⁷⁷. Therefore, the optimization strategy focused on increasing the effective Ga adatom diffusion length or mitigating its effects. Three approaches are explored:

- (i) *GaP temperature optimization.* An increase in the GaP growth temperature enhances the Ga adatom diffusion length. However, the temperature window for maintaining the GaP axial growth is limited to a $\Delta T \approx + 60$ °C, which results insufficient to produce a significant change in the tip morphology.
- (ii) *Reduction of the precursors line pressures.* Lowering the precursor line pressures decreases the probability of Ga adatom nucleation on the NW sidewalls. This approach lead to a substantial improvement in the tip

morphology. Figure A.1.1 (f) shows a TEM image of a representative NW grown with TEGa and TBP line pressures reduced to 0.40 Torr and 2.00 Torr, respectively. Under these conditions, approximately 60% of the NWs out 100 exhibits a uniform, untapered tip geometry.

- (iii) *NW length control.* A further improvement is achieved by reducing the total length of the GaAs and GaP segments, making it comparable to the diffusion

Figure A1.1.1: GaAs/GaP NW-heterostructured stems obtained from Au-film dewetting, using different growth conditions. (a) Bright-field TEM image of a single GaP tip obtained using 0.70 and 2.50 Torr of the TEGa and TBP line pressures, respectively; (b) 45°-tilted SEM image of the ensemble of NWs obtained with the same line pressures as those in panel “a”; (c) Bright-field TEM image of a GaAsP QD grown on pencil-shaped GaP, with the QD position highlighted by the red box; (d) STEM line-scan EDX, with the As profile in blue highlighting the QD presence, as well as the GaAsP tails; (e) Schematic of the QD shape obtained for unoptimized GaP tips; (f) Bright-field TEM image of a GaP tip obtained using the reduced TEGa and TBP line pressures (0.40 and 2.00 Torr, respectively); (g) 45°-tilted SEM image of the ensemble of NWs obtained using the same line pressures as those in panel “c” and shortening the GaAs and GaP growth times. The TEM images refer to single NWs transferred from the NW ensembles shown in the SEM images.



length of Ga adatoms. Literature reports¹⁸³ indicate that radial growth is a stochastic-driven process, connected to the ratio between the diffusion length of Ga along the NW sidewalls and the NW length. By limiting the overall length below the QD to less than 1 μm - which is roughly the diffusion length of Ga^{205,206} – parasitic radial growth is effectively suppressed. Indeed, by shortening the GaAs+GaP length from (1200 ± 280) nm to (940 ± 130) nm, nearly 100% of NWs exhibited the optimal tip shape, as confirmed by the SEM image in Figure A1.1 (g). Importantly, the WZ crystal phase of GaP remains free of stacking faults under these optimized growth conditions.

To further investigate the crystal structure of the GaP NWs, the unit cell is determined by three-dimensional electron diffraction (3DED)²⁰⁷. The measurements are carried out in collaboration with Prof. Mugnaioli, from CISUP University of Pisa. A STEM mode is employing using the highest spot size and a condenser aperture of 10 μm . The CL3 lens current is tuned to achieve a quasi-parallel beam on the sample, with a diameter of 30 nm. 3DED data are collected over a tilt range of $\pm 30^\circ$, with 1° steps and 0.5 s exposure time per frame, at a camera length of 250 nm. Data analysis are performed using the PETS2 software²⁰⁸. The GaP cell is determined as hexagonal primitive (hP), with lattice parameters $a = 2.89 \text{ \AA}$ and $c = 6.40 \text{ \AA}$, with the c -axis parallel to the NW growth direction.

In summary, the GaAs/GaP heterostructure is successfully optimized using growth temperature of 560°C , a line pressure of TEGa and TBP of 0.40 Torr and 2.00 Torr, respectively, and limiting the total length to (940 ± 130) nm. This optimized GaAs+GaP structure will be referred to as the “*stem*” in the following of the chapter.

A1.1.2 GaAs_xP_{1-x} ternary alloy growth calibration and QD growth.

To explore the possibility of tuning the QD composition through controlled As incorporation, a systematic calibration of GaAs_xP_{1-x} ternary alloy is performed. The study is conducted on samples grown from Au dewetted films, using the optimized stems structure described in the previous subsection. In these experiments, GaAs_xP_{1-x} segments are grown on top of the stem by varying the TBAs and TBP line pressures, while

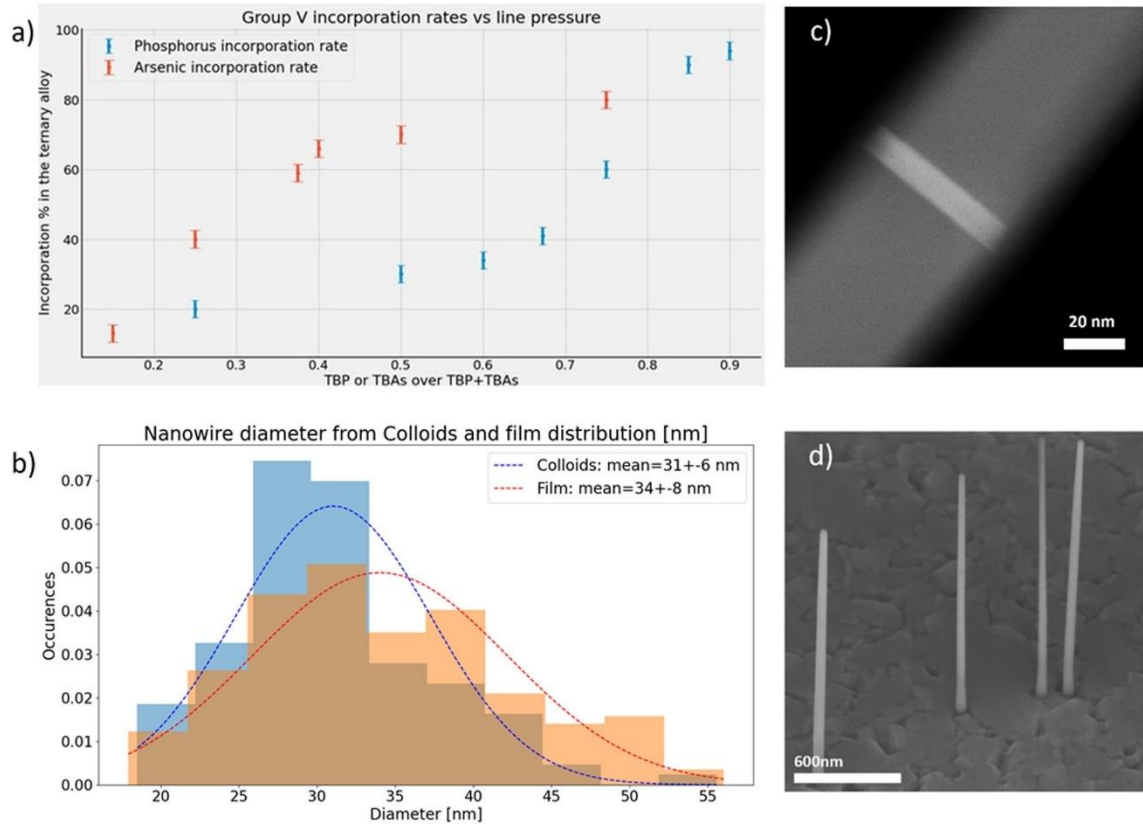


Figure A1.1.2: (a) Group V percentage in the ternary alloy as a function of the partial group V precursor line pressure measured on NWs grown from Au-film dewetting. (b) Diameter distribution of the NWs grown from colloids vs those grown from Au-film dewetting. (c) TEM image of a $\text{GaAs}_x\text{P}_{1-x}$ QD with $x = 0.90$ embedded in a NW grown from the Au 20 nm-diameter colloidal solution, where the sharp interfaces are to be noted. (d) 45°-tilted SEM image of the ensemble of NWs grown from a colloidal solution.

maintaining the TEGa line pressure constant at 0.40 Torr and fixing the total group III/V ratio at 2 for all the samples. Figure A1.1.2 (a) presents the incorporation percentages of As (in red) and P (in blue) in the resulting ternary alloy as a function of the corresponding precursor partial line pressures. The explored alloy compositions range from $x = 0.10$ to $x = 0.90$. Consistently with previous reports, the incorporation rates of P and As differ significantly, and the As incorporation does not scale linearly with TBAs partial line pressure.

After demonstrating the good control over the $\text{GaAs}_x\text{P}_{1-x}$ composition, three alloy compositions are selected for the QD growth – $x = 0.50, 0.70$, and 0.90 - all characterized by high As content. This choice is made to maximize the bandgap offset between the QD and the GaP barriers, and to explore the tunability μ -PL measurements. For reliable optical characterization, a GaP passivation shell is grown after the QD formation, since surface states are known to degrade the optical and electrical properties of the QD, leading

to severe quenching of the emitted PL signal²⁰⁹. To promote radial shell growth, a reduction in the NWs density is necessary compared to the high density ensembles obtained from Au-film dewetting. Therefore, the NW-QDs are grown starting from a low density ensemble of 20 nm-diameter Au colloids of 5×10^{-1} NW/ μm^2 , in contrast with the high density of 5×10^1 NW/ μm^2 obtained from Au film-derived ensembles. As shown in Figure A1.1.2 (b), the use of Au colloids leads also to a narrower NW diameter distribution and, consequently, a more homogeneous QD size. This also results in a more uniform NW length distribution and QD thicknesses, owing to the strong dependence of the axial NW growth and the catalyst diameter. A representative STEM image of a $\text{GaAs}_x\text{P}_{1-x}$ QD grown without the GaP passivation shell is shown Figure A1.1.2 (c), revealing a sharp interface between the QD and the surrounding GaP segments. The resulting QDs exhibit an average diameter of (40 ± 8) nm and a thickness of (12 ± 6) nm. The subsequent GaP passivation shell, grown for 30 minutes under the same conditions of the GaP tip, results in a final shell thickness of approximately 30 nm.

A1.2 Optical characterization of the QD emission

In this section, the optical characterization of the $\text{GaAs}_x\text{P}_{1-x}$ NW-QDs grown is discussed. First, the tunability from the QDs is demonstrated in Section A1.2.1. Then, the demonstration of the spatial localization of the light emitter is deepened in Section A1.2.2. Finally, power and temperature studies are discussed in Section A1.2.3.

A1.2.1 Energy emission tunability.

To demonstrate the tunability of the $\text{GaAs}_x\text{P}_{1-x}$ NW-QDs, μ -PL measurements are performed at 5.5K. As a preliminary step, the optical response of WZ GaP NWs without QDs is investigated, to identify its emission features and to distinguish them from those originating from the $\text{GaAs}_x\text{P}_{1-x}$ QDs. Figure A1.2.1 (a) reports the μ -PL spectra acquired from different positions on an ensemble of GaP NWs (spectra (i)-(iv)). All spectra exhibit similar features. An intense and broad band is centered at 1.893 eV with a FWHM of 0.500 eV (vertical dashed line). This emission is attributed to incorporation of large concentrations of impurities, likely related to the incorporation in the NW of carbon or antimony atoms, which are present as trace contaminants in the used CBE growth

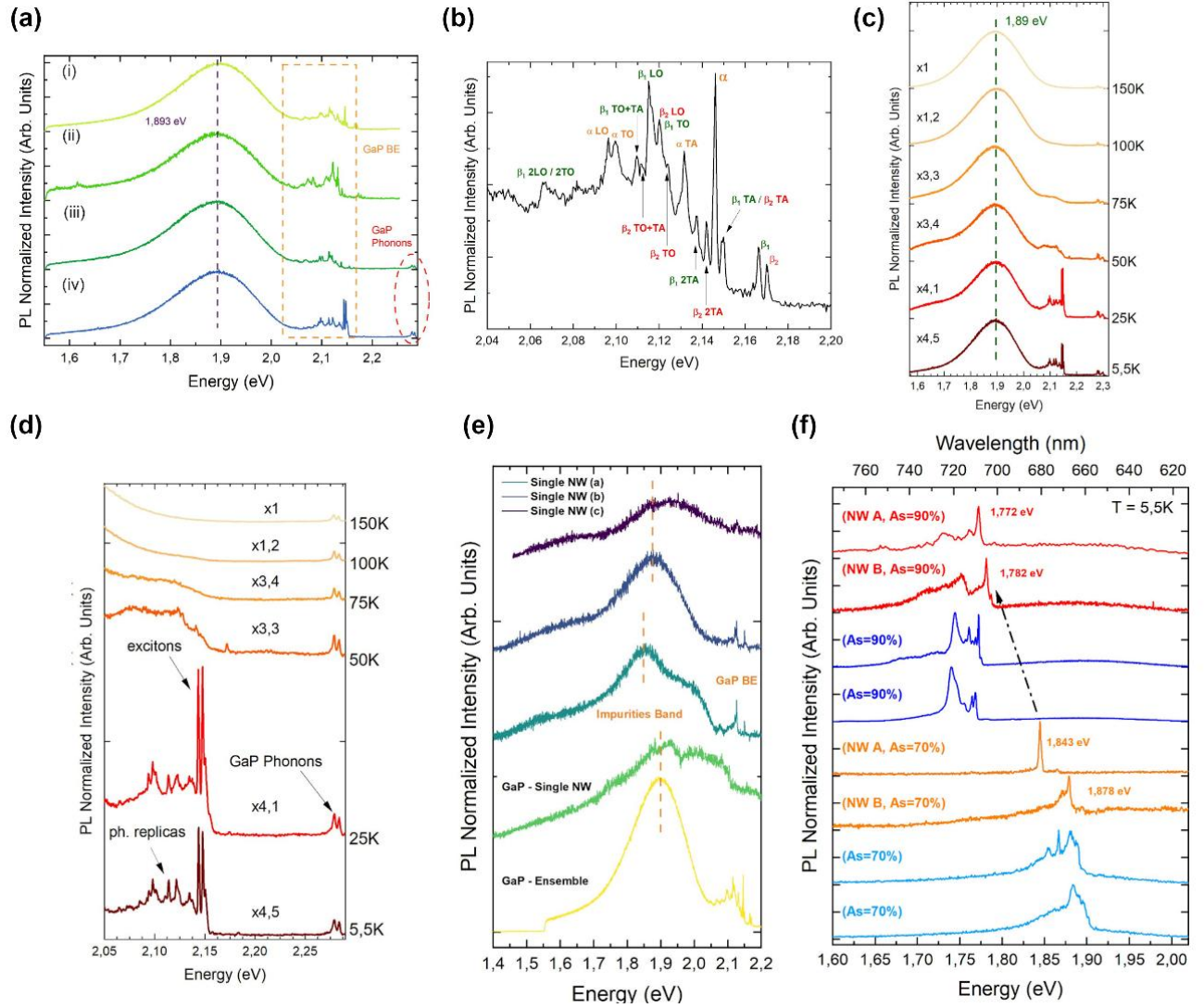


Figure A1.2.1 (a) μ -PL spectra taken with an excitation power of 500 nW on different sample points (i-iv) of an ensemble of GaP NWs (no QD). The orange rectangle highlights the GaP bound exciton region, and the red circle shows the WZ GaP LO and TO phononic modes. (b) μ -PL spectrum with an excitation power of 200 nW zoomed on the narrow excitonic lines spectral region. Phonon replica peaks are highlighted with different colors. (c) Temperature dependent μ -PL spectra on GaP NW ensemble, with the broad emission band from impurities highlighted by the green dashed line, and normalization factors are reported on the left side; (d) Zoom on the BE spectral region, showing quenching of the narrow excitonic emissions and pertinent phonon replicas. At 50 K, the impurity states do not exhibit narrow recombination peaks anymore, with only the GaP phonons remaining visible. (e) μ -PL spectra of single GaAsP QD NWs (As = 50%) compared to spectra of a single NW and an ensemble of NWs on GaP. The orange dashed lines mark the main impurities band, visible in both NWs with and without QD. (f) μ -PL spectra on ensemble (cold colors, two representative spectra for each sample, acquired on different points) and single (warm colors) GaAsP QD NWs at $T = 5.5$ K. Single NWs were manipulated and measured on silicon, with the axis parallel to the substrate, and NW ensembles were measured in the vertical position. NW A and NW B show representative spectra of two single NWs detached from the same sample, i.e., with the same As content. The emission energy redshifts as a function of the As %, as indicated by the dotted black arrow.

chamber²¹⁰. In the energy range between 2.050 eV and 2.200 eV (highlighted by the orange dashed rectangle), several narrow lines appear, originating from the recombination of shallower bound exciton states with donor/acceptor impurity atoms of, likely, C and Sb. The LO and TO phonon replicas of the WZ GaP phase are also observed at 2.279 eV and 2.284 eV (in spectra “iii” and “iv” of the panel), in agreement with both theoretical

Phonon Mode	$\Delta E(\text{meV})$	Energy (eV) - α	Energy (eV) - β_1	Energy (eV) - β_2
TA	14	2.132	2.152	2.156
2TA	27	2.119	2.139	2.143
TO	45	2.101	2.121	2.125
LO	50	2.096	2.166	2.120
TO+TA	59	2.087	2.107	2.111
LO+TA	64	2.082	2.102	2.106
2TO	90	2.056	2.076	2.080
2LO	99	2.047	2.067	2.071

Table A1. List of phonon replicas observed in Figure A1.2.1 (b). The second column reports the expected shift from the excitonic peaks due to the indicated phonon replicas. Columns three to five show the energy of each phonon replica peak related in the three BES

predictions and previous experimental data²¹¹. Figure A1.2.1 (b) shows a magnified view of the spectral region between 2.050 eV and 2.200 eV. The most intense contributions are

likely excitons bound to impurities (BE), with the peak at 2.146 eV, at 2.166 eV and at 2.170 eV labelled as α , β_1 and β_2 , respectively. Peaks α and β_1 have been previously reported in WZ GaP NWs¹⁸². The corresponding FWHM values are 1.52 meV, 1.75 meV, and 1.42 meV, respectively. At lower energies, a series of weaker peaks are detected, which can be assigned to phonon replicas of the main excitonic transitions^{182,211}. Table A1 summarizes the expected energy shifts (ΔE) from the excitonic peaks due to the replicas of the TA ($\Delta E = 14$ meV) acoustic phonon mode, and the TO ($\Delta E = 45$ meV) and LO ($\Delta E = 50$ meV) optical phonon modes, as also indicated by labels in the figure. Single NWs show similar but much weaker emission spectra. Power-dependent μ -PL measurements on the α , β_1 , and β_2 peaks reveal no red-shift and high saturation power. The integrated intensity of PL follows a power-law dependence, $I \propto (P_{exc})^M$. The extracted exponents are estimated as: $M_\alpha = (1.007 \pm 0.001)$, $M_{\beta_1} = (1.0 \pm 0.4)$, and $M_{\beta_2} = (1.33 \pm 0.07)$. The linear dependence observed for α indicates single excitonic recombination, while the superlinear behaviour of β_1 and β_2 is compatible with charged excitons formed due to inhomogeneous charge capture within the NW structure. Temperature-dependent μ -PL measurements on the GaP NWs ensembles are reported in Figure A1.2.1 (c, d). A fast quenching of the narrow emission peaks is observed while

the broad impurity band gains intensity without reaching saturation and dominates the emission above 75 K. This indicates that the radiative recombination of the narrow emission lines originates from shallower impurities (having binding energy < 5 meV) than those composing the band at 1.890 eV.

After establishing the optical signature of GaP NWs, samples containing $\text{GaAs}_x\text{P}_{1-x}$ QDs are investigated. For QDs with 50% of As content, no distinct QD-related emission peak is observed (Figure A1.2.1 (e)). The spectra are dominated by the broad band of impurities and none of the measured NWs allow to identify $\text{GaAs}_{0.5}\text{P}_{0.5}$ emission band or peaks. This behaviour can be explained by an unfavourable band alignment: preliminary calculations performed in the ZB phase indicate that the energy separation between GaP and $\text{GaAs}_{0.5}\text{P}_{0.5}$ QD bandgap is only 50 meV, which may be insufficient to create a favourable recombination center for photogenerated carriers, which instead recombine in the GaP barriers.

Subsequently, samples containing higher As ($x = 0.7$ and 0.9) content are thus analyzed. All QDs have a similar average thickness of (12 ± 6) nm. Figure A1.2.1 (f) shows representative μ -PL measured at 5.5 K. Warm colours are measured from individual NWs transferred on Si substrate, while cold colours are from the as-grown NW ensembles. The ensemble spectra reveal an emission band that characterizes the sample as a function of the incorporated As content: a clear shift is visible from 1.870 eV (As = 70%) to 1.760 eV (As = 90%). This trend is qualitative consistent with expected shift from calculations performed in the ZB phase, with predicted emission energies of 1.890 eV (As = 70%) and 1.760 eV (As = 90%). Calculations in the WZ phase are not trivial because carriers effective masses and refractive indices for the two compounds in the WZ phase are either not experimentally available or do not agree with the theory. Despite the approximation arising from considering the ZB phase, these calculations are still useful for understanding the magnitude and direction of the energy shift as a function of As % and the QD size. The ensemble emission spectra correspond to a convolution of multiple narrower lines from individual NWs. Preliminary calculations indicate that variations in QD thickness and composition both contribute to the observed broadening. Considering that the QD thickness, as measured by STEM, is (9 ± 3) nm for 90% As content and (15 ± 3) nm for 70% As content, the calculations return variations in the QD emission energy

respectively of ± 25 meV and ± 10 meV. Fluctuations in the As content in the QD can also contribute to shifting the emission from wire to wire. EDX measurements show invariance, within the experimental error of 5%, between the As content in the QDs of the same sample. Considering fluctuations in the As content by $\pm 2.5\%$, the variation in the emission energy is calculated to be ± 15 meV for 90% As content and ± 10 meV for 70% As content. Therefore, in the ensemble, fluctuations in the QD size and As content are both likely to contribute to the total FWHM. Last, because smaller QD size results in higher quantum confinement, decreasing the size of the 15 nm-thick QD (70% As content) would further increase the emission tunability range. The μ -PL spectra of individual NWs are characterized by a single narrow peak, whose energy decreases with increasing As %, as discussed for the ensemble measurements. The spectral position and FWHM of the QD peak of all single NWs in the same sample slightly vary, as discussed, and the QD peak energy resides well within the ensemble spectral emission range. Measurements on a large number of individual NWs allowed to estimate more precisely the average emission energy through the “Lorentzian” fit of the main emission peaks: (1.767 ± 0.013) eV for As = 90% and (1.858 ± 0.029) eV for As = 70%. These values are in agreement with previous measurements on GaAsP QDs in ZB GaP NWs¹²⁶, but in our work it has been estimated the As % incorporated in the QD, so it is possible to correlate the QD composition with the emission energy.

A1.2.2 Spatial localization of the light emitter.

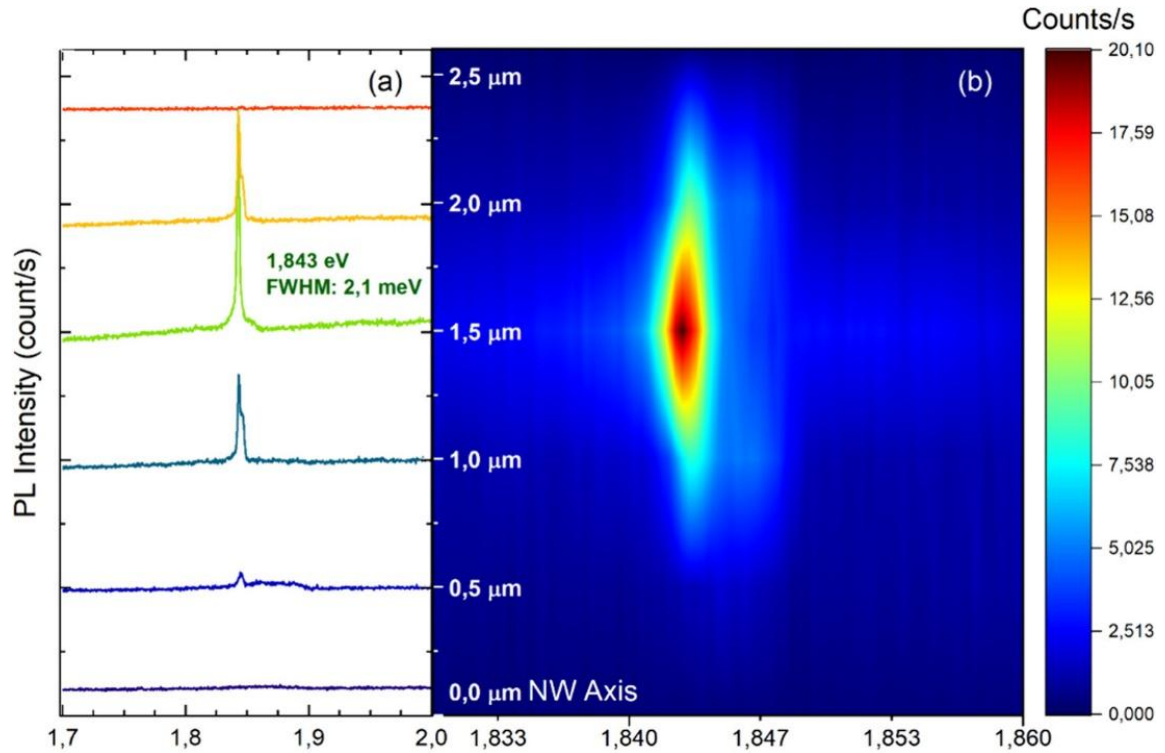


Figure A1.2.2 μ -PL measurements of a single GaAsP NW-QD with As = 70%, $T = 5.5$ K, and an excitation power of 1 μ W. (a) μ -PL spectra along the NW axis. The QD signal is visible as an intense and sharp emission line at 1.843 eV with a FWHM 2.1 meV. (b) Color plot of the intensity of the emission along the NW axis, with a close-up of the QD emission spectral range. Single spectra singled-out by this plot are shown in panel a on a wider spectral range. Measurements show the locality of the emitter, whose intensity is localized in a region smaller than 1 μ m.

To investigate the variation in emission along the NW axis and to confirm that the intense and narrow emission line observed in individual NWs originates from the QD, spatially resolved μ -PL maps are acquired on single NWs transferred on Si substrate with markers. Figures A1.2.2 presents a representative μ -PL map and corresponding spectra collected at 5.5 K under a constant excitation power of 1 μ W. The analyzed NW, approximately 2.3 μ m in length, is isolated from the ensemble of QD NWs with 70% of As. Panel (a) shows the μ -PL spectra obtained by scanning along the NW axis with 500 nm steps, from one end of the wire to the other. An intense emission line at 1.843 eV is observed (in agreement with spectra shown in Figure A1.2.1 (f)), with a FWHM of (2.1 ± 0.2) meV. The linewidth is in line with values typically reported for QD with this material system. The linewidth broadening may arise from point or line defects, interface roughness, and alloy disorder within the QD region. Moving away from the narrow QD peak, an underlying broadband emission at energies between 1.840 and 1.890 eV is observed,

probably also in this case originating from impurity states in the GaP passivation shell, such as C and Sb²¹⁰. The colour plot in panel (b) shows the spatial distribution along the NW axis of the main peak (1.843 eV). It gains intensity in a localized area with a size comparable to the QD, with the width of the spot illuminating the wire, confirming the presence of a smaller structure that is identified as the GaAsP QD. From the growth procedure, the QD is expected to be located in the approximate center of the NW growth axis, as is also visible in the μ -PL map. Hence, these measurements demonstrate again the creation of an efficient and localized carrier capture mechanism. A similar result is obtained also for the As = 90% QDs.

A1.2.3 Power and Temperature Study.

The evolution of the optical emission of single GaAsP QDs having 70% of As content is investigated as a function of both excitation power and temperature. Although experimentally challenging, this analysis provides valuable insights into the nature of the emitting states and their energy distribution. Figure A1.2.3 (a) shows μ -PL spectra as a function of the laser power, with given normalization factors highlighting the gain in intensity as the excitation power increases. Measurements are carried out on the same QD presented in Section A1.2.2. Below the power of $P_0 = 1 \mu\text{W}$, the spectra are dominated by a narrow band composed of two main emission lines. At low excitation powers ($<0.2P_0$), the high-energy peak at 1.846 eV dominates the spectrum. Its intensity saturates around $0.5P_0$ and exchanges intensity with the low-energy peak at 1.843 eV. The latter becomes dominant at P_0 , and at this power, which is the characteristic spectrum presented in the map of Section A1.2.2. The integrated intensities of both peaks are fitted according to the power $I_{\text{exc}} \propto (P_{\text{exc}})^M$, as shown in Figure A1.2.3 (b.2), for powers below P_0 . The lowest energy peak exhibits a slope $M_X = 1.07 \pm 0.06$, consistent with a single exciton recombination process (thus, that peak is labelled as a free exciton, X). This assumption is further confirmed by the invariance of its emission energy as a function of the excitation power (dashed line labelled X in panel (a)) and by the saturation of emission at high excitation power presented and fitted in panel (b.1). The higher energy state (1.846 eV), in contrast, follows a power law slope of 1.47 ± 0.16 , suggesting the involvement of a charged exciton (X^* , positive or negative) resulting from the unequal capture of photoexcited carriers in the QD²¹². As shown in Figure A1.2.3 (a), at higher excitation

powers, the population of high-energy states is also observed²¹². At $2P_0$, a peak of 1.852 eV starts to gain intensity without red shifting. The integrated intensity fit for this contribution yields a power law coefficient of 2.3 ± 0.1 ; therefore, this peak is attributed to a biexcitonic recombination process (XX; see the dashed line in panel (a)). A double peak centered at 1.887 eV arising at P_0 is also observed and gaining in intensity with

increasing power. This peak is visible in most of the single NWs measured and could originate from radiative recombination from excitons in the p-shell states of the QD²¹³. The integrated intensity trend fitted with the power law yields 1.01 ± 0.05 eV for the peak at 1.886 eV and 1.15 ± 0.05 eV for the peak at 1.889 eV, respectively. At $50P_0$,

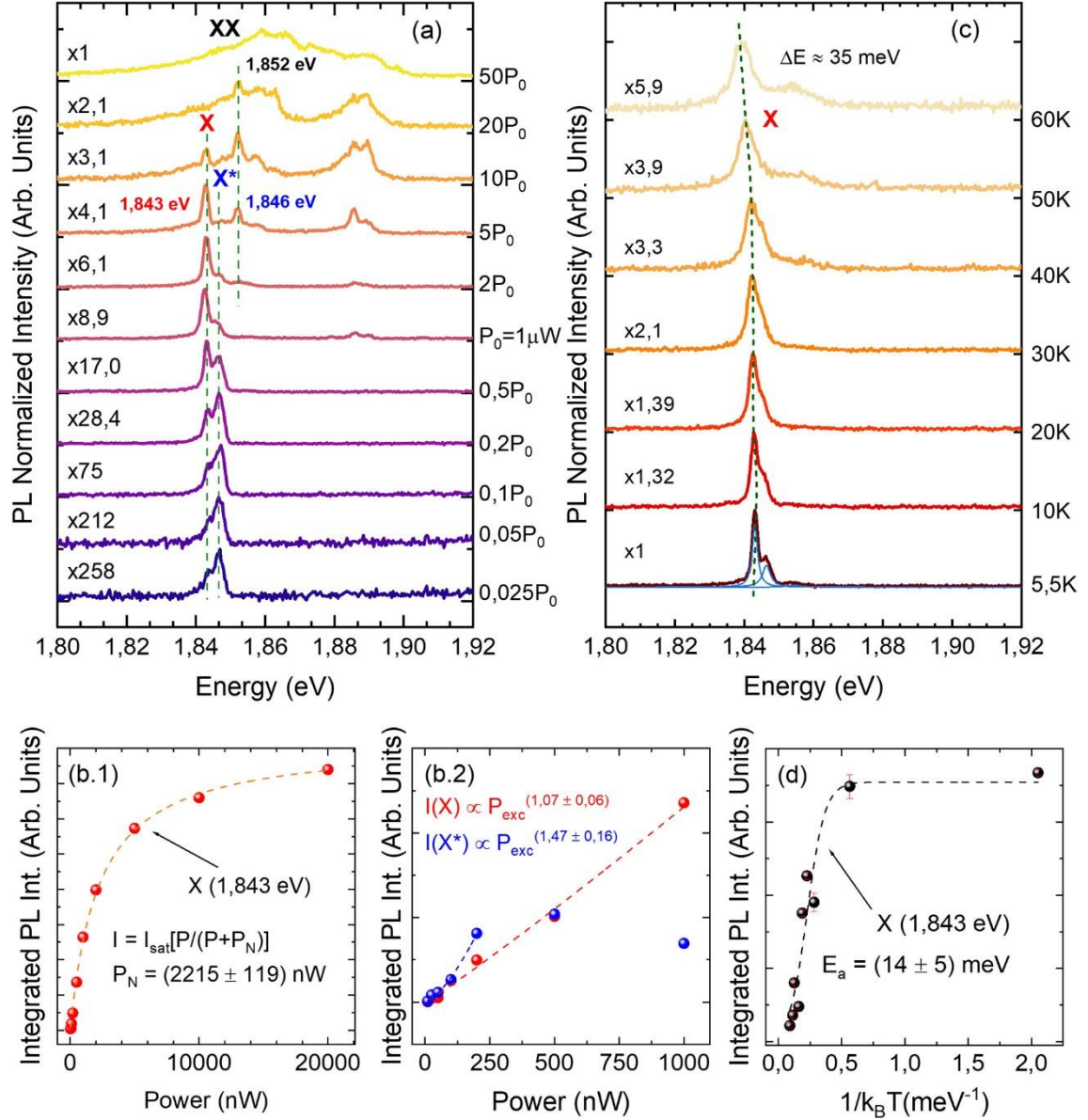


Figure A1.2.3: Power- and temperature-dependent μ -PL measurements on single GaAsP QD NWs with As = 70%. (a) Power-dependent spectra of the QD peak acquired at 5.5 K, with intensity normalization factors indicated on each spectrum. Dashed lines highlight the single exciton (X), charged exciton (X*), and biexciton (XX) emission peaks. $P_0 = 1 \mu W$. (b.1) Plot of the integrated intensity (obtained from the spectra in panel a of peak X as a function of the power. The dashed line shows a fit with $I = I_{sat} [P / (P + P_N)]$, where P_N is the laser power at which the intensity is half of I_{sat} . (b.2) Power-dependent integrated intensity of X (red dots) and X* (blue dots) at powers below P_0 to show the X* saturation curve and X linear behavior. (c) Temperature-dependent μ -PL spectra, acquired at P_0 , with normalization factors. The blue curves under the 5.5 K spectrum show the Lorentzian curves used to fit each peak. The green dashed line highlights the thermal red shift of the emission. (d) Integrated PL intensity of the X peak as a function of the reciprocal of the temperature with the Arrhenius fit (dashed line) and extracted activation energy.

multiexciton processes start to gain in intensity and do not allow us to spectrally resolve single peaks²¹².

Figure A1.2.3 (c) reports the temperature-dependent measurements of the same NW-QD, evidencing the expected thermal quenching of the emission as the temperature rises. The X peak broadens and loses intensity as temperature increases, as expected for a single free exciton. The energy states related to higher energy emission start to populate with photogenerated carriers because they gain thermal energy with an increase in the temperature, and at around 40 K, it is no longer possible to spectrally resolve X from the other contributions to the emission spectrum (such as the X* peak). As a result, the emission broadens (a FWHM of 7.4 meV at 60 K) and undergoes an expected thermal redshift with a Varshni-like behavior^{214,215} of 35 meV from 5.5 to 60 K. The “Arrhenius” plot of the integrated PL intensity of the X peak in panel (c) is shown in panel (d). The data are fitted considering one active nonradiative recombination channel for the exciton: an activation energy $E_a = (14 \pm 5)$ meV is estimated, suggesting that, due to the thermal energy, carriers escape to an excited state located ~ 14 meV beyond the free exciton, most likely the biexciton, also visible in the power study at high powers and in the temperature study at temperatures above 40 K.

A1.3 Summary and conclusions

In this chapter, the growth and optical properties of WZ GaP NWs embedding single GaAs_xP_{1-x} QDs have been investigated. A high degree over both the QD morphology and chemical composition has been achieved. Single-NW μ -PL measurements reveal that the emission is dominated by a narrow peak whose energy position shifts according to the As content of the QD. This tunability demonstrates the potential of the system as a composition-controlled quantum light source. μ -PL mapping along the NW axis confirms the attribution of this peak to the QD and highlights the realization of a localized and efficient carrier recombination mechanism that promotes emission from the QD rather than from the GaP NWs. Power-dependent measurements revealed the presence of two radiative mechanisms contributing to the QD emission. In the low-excitation-power

regime, the spectrum is dominated by the emission of a charged exciton. This feature loses intensity as we raise the excitation power, while the single free exciton gains in intensity. Finally, the study of the QD emission as a function of the temperature shows quenching and a Varshni-like shift of the main peak. However, the peak bandwidth is still <8 meV at 60 K.

Overall, these findings demonstrate that high-quality and spectrally-tunable light emitters can be realized through optimization of the growth process. The results underline the potential of these novel WZ $\text{GaAs}_x\text{P}_{1-x}$ QD NWs with tailored composition to advance applications in quantum optics and photonics in the future.

Appendix A2: References of Figure 2.2

In this appendix, the references of the points in Figure 2.2 are provided with the corresponding numbers in the figure:

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List of Abbreviations

ACE	Acetone
CBE	Chemical Beam Epitaxy
DE-QDs	Droplet Epitaxy Quantum Dots
DI-water	De-Ionized water
EDS	Energy Dispersive X-Ray Spectroscopy
FDTD	Finite-Difference Time-Domain
FFT	Fast Fourier Transform
FSS	Fine Structure Splitting
FWHM	Full-Width Half-Maximum
GI	Growth Interruption
HAADF	High-Angle Annular Dark-Field
HH	Heavy Holes
IPA	Isopropyl alcohol
LH	Light Holes
MBE	Molecular Beam Epitaxy
MO	Metal-Organic
MOCVD	Metal-Organic Chemical Vapor Deposition
MOVPE	Metal-Organic Vapour-Phase Epitaxy
NP	Nanoparticle
NW	Nanowire
NW-QDs	Nanowire Quantum Dots
PML	Perfectly Matched Layer
QD	Quantum Dot
RF	Radio Frequency
RHEED	Reflection High-Energy Electron Diffraction
SAE	Selective Area Epitaxy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SF	Stacking Fault
SK-QDs	Stranski-Krastanov Quantum Dots
STEM	Scanning Transmission Electron Microscopy

TBAs	TertiaryButyl Arsine
TBP	TertiaryButyl Phospine
TDMASb	Tris(dimethylamido)antimony
TEGa	Triethylgallium
TEM	Transmission Electron Microscopy
TMIn	Trimethylindium
UHV	Ultra-High Vacuum
VLS	Vapor Liquid Solid
VSS	Vapor Solid Solid
WZ	Wurtzite
ZB	Zincblende
μ-PL	Micro-Photoluminescence
3DED	Three-Dimensional Electron Diffraction

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