Growth of hexagonal group-IV semiconductor nanowires

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Front-and-back page: Top-down scanning electron microscopy image of core/shell nanowires with a hexagonal crystal structure Si shell, viewed along the <0001> direction.
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Chapter 1 – Introduction

Digital electronics based on silicon (Si) technology have contributed to profound developments in almost every human endeavor and a boom in world economic growth in the late 20th and early 21st centuries. This has been most clearly demonstrated by Moore’s law\(^1\), which noted a trend towards the doubling of the number of components per integrated circuit every two years. This exponential growth has held up for half a century already, since its publication by Gordon E. Moore in 1965. Nanotechnology, the technology of nanostructures where the dimensions are in the \(10^{-9}\) m range, has been the driving force behind this. At these length scales a whole new field has opened, as it was predicted by Richard P. Feynman’s 1959 lecture “There’s plenty of room at the bottom”\(^2\). Two main paths for the fabrication of nanostructures have been identified. The top-down approach creates nanoscale devices by the intentional breaking down of a system. This is implemented by using large, externally controlled microfabrication devices and methods, like lithographic processes and etching techniques. The other path, the bottom-up approach, creates systems by piecing together smaller units to create a larger complex. This is practically implemented by using atoms and molecules as building blocks, taking advantage of their chemical properties, to cause them to self-assemble into the desired structures. The growth of thin films and nanowires can be achieved via either path; in this thesis, we will focus on the bottom-up approach.

1.1 State of the Art

At the heart of digital electronics is its fundamental building block, the Si-based transistor. These fundamental building blocks can be organized en masse, or integrated, into an integrated circuit (IC). In order to make faster and smaller electronic devices, like those found in computers, smart phones and tablets, we need to pack\(^1\) more and more transistors onto ICs. But there is an ultimate limit as to how much computing power can be done with Si-based electronics, set forth by the laws of thermodynamics and quantum mechanics. The two fundamental limiting factors are heat dissipation and current leakage, respectively.

By the addition of an ever-growing number of transistors in ICs, heat dissipation due to Joule heating becomes a critical issue. This leads to power loss and noise. The power loss occurs due to energy being consumed to significantly heat up the device and the electronic noise (Johnson-Nyquist noise) leads to random fluctuations in the electrical signal.

As previously mentioned, the other negative aspect of this addition of transistors is current leakage. This is a result of the fact that in order to fit more
and more transistors in an IC, the transistor size is becoming constantly smaller and smaller. The International Technology Roadmap for Semiconductors predicts that by around year 2021 we will have practical electronic devices working at the 5 nm node. At this size scale, the laws of quantum mechanics start to play a significant role. The drawback is that transistors smaller than the 7 nm node will experience quantum tunneling through their logic gates, leading to current leakage. This leads us to believe that the process scale of 5 nm may very well represent the end of Moore's Law for scaling of electronic devices.

1.1.1 Semiconductors

Si is a semiconductor and these are materials that exhibit a crystalline or amorphous nature and display resistance characteristics that lie in-between those of typical conductors and insulators. Their resistance decreases as their temperature increases, which is a behavior opposite to that of metallic conductors. A critical characteristic of semiconductors is that we have the ability to deliberately introduce impurities (doping) into their crystal structure, in order to tune their conductive properties in advantageous ways. If the impurity atoms have an extra electron compared to the atoms of the semiconductor they are doping, then the semiconductor has more free electrons as charge carriers and is called “n-type”. If, on the other hand, the dopant atoms have an electron less, then the semiconductor is known as “p-type” and has more free holes as charge carriers. These holes are essentially an “absence” or a lack of an electron and behave as a charge carrier as well. The doping consequently results in a decrease of a semiconductor’s resistance and further allows the fabrication of junctions between differently doped regions of a semiconductor. This is the basic principle behind transistors, diodes and essentially all modern electronics. Semiconductor-based devices like these, can exhibit several important technological properties, like the ability to allow (or not) the passing of a current, variable resistance and interaction between their electrical properties with light and heat.

1.1.2 Classes of Semiconductors

The different classes of the most important semiconductors that can be distinguished are elemental semiconductors and compound semiconductors. These come from the groups- II, III, IV, V and VI of the periodic table of the elements. Elemental semiconductors originate mostly from group-IV, like Si and germanium (Ge), and group-VI. Compound semiconductors are made up of combinations from the other groups and can be binary, ternary or even quaternary, made by a combination of two, three or four elements respectively. Compound semiconductors that are relevant to this work are those made by a
combination of group-III and group-V (III-V semiconductors) like gallium arsenide (GaAs) and gallium phosphide (GaP). III-V’s can be fabricated both as n- and p-type by doping them with e.g. sulfur (S) or zinc (Zn) respectively, have high carrier mobility and direct energy gaps which make them ideal for optoelectronic applications. Unfortunately, they are expensive. Si on the other hand, is cheap, robust and easy to process. This results in the domination of contemporary technology by Si.

1.1.3 Semiconductor Band Structure

Crystalline semiconductors can be described by their electronic band structure which specifies the range of energies that a charge carrier may have (energy bands) or not (band gaps). This arises by taking advantage of the periodic lattice of a crystal in which an electron interacts with the periodic potential generated by the positive lattice ions. A result of this is that the forbidden energy gaps (band gaps) can be described as either being direct or indirect. In the case of a direct gap the lowest energy state above the gap is at the same horizontal position as the highest state below the gap (see Fig. 1.1a and for a real semiconductor –GaAs–, see Fig. 2.5a). This basically means that the energetic transition of a charge carrier from an energy state below the gap to an energy state above the gap (or vice-versa) is more likely to happen. The direct nature of a semiconductor’s band gap makes it a likely candidate for efficient light interaction as we will see further ahead (see Ch. 2.2.2). On the contrary, in the case of an indirect gap, the lowest energy state above the gap is at a different horizontal position than the highest state below the gap (see Fig. 1.1b and for two real semiconductors –Si and Ge–, see Figs. 2.5b and 2.5c). This means that

![Figure 1.1. Schematics of (a) a direct band gap and (b) an indirect band gap. Adapted from Ref. 4]
the energetic transition of a charge carrier from an energy state below the gap to an energy state above the gap (or vice-versa) is less likely to happen. Thus, an indirect band gap semiconductor will interact rather inefficiently with light.

1.1.4 Optoelectronic Devices

Optoelectronic devices are essentially electronic devices, especially semiconductor-based, in which their electronic properties can interact with light, essentially making them electrical-to-optical (and vice-versa) transducers. As mentioned previously this is the case for direct band gap semiconductors. The interaction process can be described in a simple fashion as the ability of a charge carrier to absorb the energy of a photon and transition from the highest allowed energy state below the gap (the states below the gap comprise the valence band) to the lowest allowed energy state above the gap (the states above the gap comprise the conduction band). This energy absorption leads to charge carriers that are free to move in the conduction band, basically adding to the conductivity of the semiconductor. On the contrary, charge carriers that reside in the conduction band of a direct band gap semiconductor, are able to emit energy in the form of a photon and transition to the valence band. Great materials for optoelectronic applications are the III-V semiconductors, but their chief drawback is their cost.

1.1.5 Photonic Integration

A proposed solution to the ultimate end of Moore's law are photonic integrated circuits (PICs) that utilize photons instead of electrons and have promised a higher bandwidth than conventional electronic integrated circuits and an absence of the Joule effect. An efficient light-emitting source is at the root of this. For the time being, the most widely utilized material for PICs is indium phosphide (InP; belongs to group III-V) that has been fabricated into both active and passive PIC components. This has in a significant amount been pioneered at the COBRA Research Center for Integrated Nanophotonics at the Eindhoven University of Technology. But in reality though, we have an industry that is almost completely based on Si due to the affordability (as compared to the expensive III-V's), the easy processability, superior structural properties, and tremendous amount of knowledge that we have gained about Si. One idea has been to integrate optically active III-V components onto a Si-based chip, but that has proven difficult because they generally exhibit a lattice mismatch with Si, thus making them difficult to integrate with Si. So, in the end, the ideal solution would be to have an optically active Si part.
Unfortunately, bulk Si which possesses the diamond cubic crystal structure and which is utilized in contemporary technology, has a notorious and well-established indirect bandgap\textsuperscript{5}, even though most semiconductors are direct gap materials. This indirect band gap makes Si rather inadequate in terms of its interaction with light. There have been several attempts to engineer a solution to this problem, such as intrinsic and alloy-induced luminescence\textsuperscript{6}, radiatively active impurities\textsuperscript{7,8} and quantum confined structures\textsuperscript{9,10}. The main issue here is the practicality of the solutions due to the decrease in emission with increasing temperature. Even though they do allow light emission, they are not necessarily practical and it may not be possible to use these effects in the production of practical devices especially with efficient optical emission at room temperature.

1.2 Place of the Thesis Within the State of the Art

On the contrary, Si with the hexagonal crystal structure is predicted to exhibit a different band structure than its cubic crystal structure counterpart. This is due to a change in the positions of the atoms and the symmetry of the hexagonal crystal (as compared to the cubic structure), which leads to a difference in the periodic potential that the charge carriers move in, as discussed previously. It will still probably exhibit an indirect band gap, but in any case, holds a promise for development, as we will discuss. Moreover, Ge with the hexagonal crystal structure is expected to possess a direct band gap, in contrast to its cubic counterpart, which is indirect. The direct nature has an important impact, in that it will interact with light much more efficiently. Furthermore, the combination of hexagonal Si and Ge into a hexagonal SiGe alloy could result in a direct band gap semiconductor. This is expected to happen at about 65\% Ge, so for a stoichiometry of around $Si_{1-x}Ge_x = Si_{0.35}Ge_{0.65}$ (further discussed in Ch. 2.2.4 and Fig. 2.7). More specifically, it is possible that the direct band gap nature of SiGe will not only make it efficient at interacting with light, but also that this will take place around the wavelength of 1.7 $\mu m$. This is important because it is relatively close to the critical wavelength of about 1.55 $\mu m$ that is colloquially known as the telecommunication wavelength, the reason being the low absorption characteristics of the optical fibers used in telecommunications for this wavelength. This makes the fabrication of hexagonal Si, Ge and SiGe highly desirable. In this thesis, we will present the realization of the growth of single-crystalline hexagonal Si, hexagonal Ge and hexagonal SiGe alloys with a stoichiometry well above $Si_{0.35}Ge_{0.65}$.
1.3 Hexagonal Si Crystal Structure - State of the Art

There have been notable efforts to fabricate hexagonal Si from a variety of perspectives. In these experiments, control of the deposition, crystal purity and growth conditions was of various degrees. Bandet et al. observed hexagonal Si crystals within a plasma-deposited thin film consisting of a mixture of amorphous silicon oxide (SiO₂), cubic Si and hexagonal Si. Fig. 1.2 depicts a cross-section of this film and an electron diffraction pattern of a hexagonal crystal\textsuperscript{11}. Even though these experiments allow the first investigation of the hexagonal crystal structure, the main issue is the lack of control over the location, volume fraction and crystalline perfection of the hexagonal grains, an issue that has troubled many other studies as well.

![Hexagonal Si Microcrystallites](image)

**Figure 1.2.** Hexagonal Si Microcrystallites. (a) TEM image showing a cross-section of a Si grain of 0.4 $\mu$m; (b) Micro-diffraction pattern of a hexagonal Si grain. Adapted from Ref.\textsuperscript{11}

Other approaches were carried out by high-pressure studies with the diamond anvil cell technique on cubic substrates\textsuperscript{12,13} and a number of experiments to grow hexagonal Si nanowires via the use of the catalyst-mediated vapor-liquid-solid (VLS) growth method\textsuperscript{14-17}. In these experiments, the control of the formation of the hexagonal crystal structure of Si has been a challenge. Most importantly, recent studies\textsuperscript{18-20} have been cautioning on the interpretation of transmission electron microscopy (TEM) diffraction patterns obtained from what is claimed to be hexagonal Si. It has been most strongly pointed out that diffraction patterns that seemingly arise from single crystalline hexagonal Si, most probably originate from defected cubic Si. This will be explained in Ch. 5 in more detail.
This means that up to date, it cannot be ruled out that single-crystalline, defect-free hexagonal Si with controlled long-range growth may actually not have been realized.

1.4 Scope of the Thesis

In this thesis, we will present the controlled and reproducible growth of hexagonal Si, Ge and SiGe on large substrate surface areas along with detailed characterization with various techniques.

This thesis consists of 7 chapters, including the introduction.

In Chapter 2 the theoretical background of the thesis will be examined; the band structure of cubic Si and Ge in comparison to the band structure of hexagonal Si and Ge, a prediction of the band structure of hexagonal SiGe as well as an in-depth analysis of the hexagonal crystal structure. Thin film deposition and the various growth modes will be discussed along with nanowire growth and nanowire heterostructures.

In Chapter 3, the experimental methods and techniques for growth and characterization will be scrutinized; nanoinprint lithography that is used to fabricate arrays of catalysts on substrates and the consequent growth of nanowires and heterostructures in the metal-organic vapor phase epitaxy (MOVPE) reactor; the scanning electron microscopy (SEM) that is used to image these structures in high magnification after growth; TEM that is used to further magnify and explore the structure in order to verify the crystal structure as well as for local chemical identification at the nanoscale; X-ray diffraction (XRD) that is utilized to calculate to a very high degree of accuracy the fundamental spacing of the atoms in the crystal lattice; the Raman spectroscopy that is further used to verify the crystal structure.

In Chapter 4 we will essentially show the growth evolution leading to the single-crystalline phase through the showcasing of a new type of defects for NWs that arose in the process and the subsequent gain of knowledge as to how to proceed in order to achieve the defect-free structure. The first observation of this type of defects in NWs, identified as crack defects, will be characterized and a model as to why they are generated in the hexagonal structure of Si will be presented.

In Chapter 5, the controlled and reproducible growth and characterization of single crystalline hexagonal Si will be presented, taking into account all the recent studies about how to unambiguously identify the phase.

In Chapter 6, the growth and characterization of hexagonal SiGe of a single-crystalline nature will be discussed, through a large range of stoichiometry.
In Chapter 7, the fabrication and description of single crystalline hexagonal Si and SiGe nanowires will be displayed. This is implemented by the growth of branches on nanowire stems, in an attempt to achieve a high amount of material, critical for optical studies, and overcome any strain buildup issues, as well as any unwanted doping from the substrate.
Chapter 2 - Theory – Background

In the following we will discuss the theory and the background of the thesis. Theoretical calculations of the band structure of Si and Ge predict significant changes from the cubic crystal phase to the hexagonal crystal phase. Ge is predicted to transition from an indirect band gap material in the cubic phase to a direct band gap material in the hexagonal phase, while Si is predicted to remain indirect in both cases, albeit with important modifications in the hexagonal band structure.

2.1 Crystal Structure

The crystalline structure of a semiconductor is important, because it determines its electrical, optical and thermal properties. The paramount characteristic of the crystal structure is its periodicity, which means that the atoms of the crystal form a regular lattice. This has an important consequence; we are essentially able to describe the whole structure by defining a fundamental unit. This unit is called the unit cell. In order to construct a unit cell, two things are needed; a description of all the symmetries and geometric characteristics and a base of atoms. The first is an abstract mathematical concept that encompasses all the geometric characteristics of the crystal and utilizes symmetry elements, condensed into a basic unit cell and is known as a Bravais lattice. The second is the atom base, *i.e.* a number of atoms –of the same kind or different– that when positioned in the points of symmetry of the Bravais lattice, results in a unit cell and which can further be used to construct the whole crystal by simple (vector) additions. In this thesis, we will mainly focus on two crystal lattices; the diamond cubic and the hexagonal diamond. Both of these structures were first observed in the diamond allotrope of carbon (C), hence the term “diamond”.

2.1.1 The Diamond Cubic Crystal Structure

The diamond cubic crystal structure is a cubic crystal structure\textsuperscript{23}. The cubic crystal structure has a unit cell in the shape of a cube and has three main varieties:

- Primitive cubic, which consists of one atom in each corner of the unit cell.
- Body-centered cubic, which is like the primitive cubic, but in addition has an atom at the center of the unit cell.
- Face-centered cubic (FCC), which is like the primitive cubic, but in addition has atoms at the centers of the faces of the unit cell. The FCC lattice is one of the two lattices that achieves the highest packing density...
and thusly are termed close-packed; the other one being the hexagonal close-packed (HCP).

We will spend a little bit of time at this point on the FCC and the HCP, as these are central to this work. Their most basic difference lies in the stacking sequence of their atomic layers. For instance, let’s assume the model of tight packing of spheres corresponding to atoms. If an initial reference layer is denoted as “A”, then the next layer of spheres on top (“B”), can be placed in the positions in the gaps in between three touching spheres from the A-layer below (Fig. 2.1). The critical difference of FCC and HCP stems from the packing of the third layer, because the spheres can again be placed in the positions in-between the gaps of three touching spheres from the B-layer below, but in two distinct fashions:

- Firstly, in such a way so that the spheres of the third layer lie in positions that are not exactly above the A-layer, in which case the layer is termed as a C-layer to denote this different position. This results in a stacking sequence of ABCABC... and corresponds to the FCC lattice.
- Secondly, in such a way so that the spheres of the third layer lie in positions that are exactly above the A-layer, in which case the layer is an A-layer again. The results in a stacking sequence of ABABAB... and corresponds to the HCP lattice.

**Figure 2.1.** Model of close-packing of spheres. The A-layer is denoted by the blue spheres, while the positions of the B-layer atoms are denoted by the red “x”. There are two options for the third layer, either the positions noted by green crosses, which is a C-layer, or in the positions noted by small green spheres, which are directly above the A-layer and thus is an A-layer in itself. In the first case the crystal structure has a stacking of close-packed spheres of the ABCABC... type, resulting in the FCC structure, while in the second case the crystal structure has a stacking of the ABABAB... type, resulting in the HCP structure.
The *diamond cubic crystal structure* is based on the FCC lattice and is basically a combination of two interpenetrating FCC sub-lattices displaced along the diagonal of the cubic cell by $\frac{1}{4}$ the length of the diagonal. The unit cell of the diamond cubic crystal structure can be seen in Fig. 2.2a. The term diamond cubic is used when all the lattice points are occupied by the same type of atoms. On the other hand, if each sub-lattice is occupied by its own type atom, then we end up with the *zincblende structure* (Fig. 2.2c), the structure in which most III-V crystallize in.

### 2.1.2 The Hexagonal Diamond Crystal Structure

The *hexagonal diamond crystal structure* is correspondingly based on the HCP lattice and is also a combination of two interpenetrating HCP sub-lattices. The unit cell of the hexagonal diamond structure can be seen in Fig. 2.2b. The term hexagonal diamond is used when all the lattice points are occupied by the same type of atoms. On the other hand, if each sub-lattice is occupied by its own type atom, then we end up with the *wurtzite structure* (Fig. 2.2d). Since the hexagonal diamond and diamond cubic crystal structures are based on the FCC and HCP lattice respectively, they are structurally closely related in that the two systems differ only in the relative placements of their close-packed layers, as can be observed from Fig. 2.1.

![Figure 2.2](image) The unit cells of (a) the diamond cubic crystal structure, (b) the hexagonal diamond, (c) the zincblende and (d) the wurtzite. (a) and (c) on one hand, and (b) and (d) on the other, have the same structure, but in (a) and (b) the lattice points are occupied by the same type of atoms, while in (c) and (d) each sub-lattice is occupied by its own type of atoms. Hence the different terms used to denote them. Note the combination of the Bravais lattice and the base, so that two atoms with a specific distance and angle between them occupy each point of the Bravais lattice. Adapted from Ref. 24
As witnessed in Fig. 2.3a, when looking in the [110] crystallographic direction (Miller indices used for the cubic system) the ABCABC... stacking of the diamond cubic crystal structure is evident, while in the equivalent [1120] crystallographic direction (Fig. 2.3b) (Miller-Bravais indices used for the hexagonal system) the ABABAB... stacking of the hexagonal diamond crystal structure is evident.

Figure 2.3. (a) Diamond cubic crystal structure viewed along the [110] zone axis. The ABCABC... stacking can be seen (first ABC stacking within the red rectangle); (b) hexagonal diamond crystal structure viewed along the [1120] zone axis, which is equivalent to the cubic [110] direction. The characteristic ABABAB... stacking can be seen (first AB stacking within the red rectangle). Adapted from Ref.25

A few words now on the naming of the structures that we have seen in Figs. 2.2 and 2.3 and described in Ch. 2.1.1 and the current one. There seems to have been some confusion on this issue where in several studies different terms have been used for the same structure and sometimes even wrong terms. Zinc sulfide (ZnS) is an inorganic compound that exists in two main crystalline forms, the more stable and thus more frequently encountered cubic one and the less frequently encountered hexagonal form. The cubic mineral of ZnS is known as sphalerite or zincblende and the hexagonal one as wurtzite. Because these two structures were first discovered in these two minerals of ZnS, the structures themselves were named after the minerals. So, in the case where we have a crystal structure that consists of a combination of two interpenetrating FCC sub-lattices displaced along the diagonal of the cubic cell by $\frac{1}{4}$ the length of the diagonal, the corresponding structure was named a zincblende structure, while for the same case of two interpenetrating HCP lattices, the corresponding structure was named a wurtzite structure. But ZnS is made up of two atoms, so one of the two interpenetrating lattices consists of one type of atom, while the other of another type of atom. This can be seen in Figs. 2.2c and 2.2d, for the zincblende and wurtzite structures, respectively. Now the same structures can
have the two interpenetrating lattices occupied by the same type of atoms. This was observed to be the case for diamond (C), where the structure was named the diamond cubic and is equivalent to the ZnS, but just with one type of atom. In the other case, it was observed that C atoms could occupy positions equivalent to the wurtzite structure (but in this case, only one type of atoms), essentially an allotrope of C. Logically, in this case it was named hexagonal diamond. This form of C was first observed in 1967 in the Canyon Diablo meteorite and thought to have been formed due to high temperature and pressure during impact with the earth’s surface.\textsuperscript{26,27} Furthermore, the discovery of hexagonal C formed during hyperbolide impacts on the planet’s surface is considered as proof of those impacts. Recently, based on this, the Younger-Dryas Impact Hypothesis was challenged by showing a lack of evidence of hexagonal C in sediments.\textsuperscript{28} Other terms encountered in literature are: “lonsdaleite” in honor of Kathleen Lonsdale a British crystallographer, “2H” (from Ramsdell notation) or “IV” crystal structure. The term that has been used somewhat wrongly is “wurtzite” since wurtzite refers to a crystal with two types of atoms and not one, which is the case of Si. In this thesis, we will show for the first time that Si and SiGe can also adopt this crystal structure.

### 2.2 Band Structure Theory

Solving the Schrödinger equation for a single electron in this case, gives Bloch waves as solutions:

\[ \Psi(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u(r) \]

where \( \Psi(r) \) is the Bloch wave, \( \mathbf{r} \) is the position vector, \( \mathbf{k} \) is the crystal wave vector and \( u \) is a periodic function with the same periodicity as the crystal.

In order to formulate a description of a system of ions and electrons, our formulation has to be quantum mechanical. We have to solve the many-body Schrödinger equation:\textsuperscript{29}

\[ \mathcal{H}\Psi(\{\mathbf{R}_i; \mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_i; \mathbf{r}_i\}) \]

where \( \mathcal{H} \) is the hamiltonian of the system, \( E \) is the energy of the system, \( \Psi(\{\mathbf{R}_i; \mathbf{r}_i\}) \) is the many-body wave function that describes the state of the system, \( \{\mathbf{R}_i\} \) are the positions of the ions and \( \{\mathbf{r}_i\} \) are the variables that describe the electrons.

The expanded form of this equation has many terms: Coulomb interactions between electrons, Coulomb interactions between electrons and ions; all these make the system highly complicated. Thus, several approximations are needed to make it simpler. Firstly, due to the big difference in mass between the ions and the electrons (three to five orders of magnitude) the ions can be treated as stationary. This is known as the Born-Oppenheimer approximation:
\[ \mathcal{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i V_{\text{ion}}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{i,j(i\neq j)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \]

where \( \hbar \) is the “reduced Planck constant” given by \( \hbar = \hbar/2\pi \), \( m_e \) is the electron mass, \( V_{\text{ion}} \) is the total external potential experienced by an electron due to the presence of the ions and \( e \) is the charge of the electron. The first term of the above equation is the electron kinetic energy, the second is the total (external) ionic potential experienced by the electrons and the third is the total potential energy by the electrons interaction with each other (due to the repelling force between them). Even with these simplifications, solving for \( \Psi(\{\mathbf{r}_i\}) \) is still an extremely difficult task. So, in order to continue, further approximations are deemed necessary. The single-particle approximation is an appropriate picture that can still be used to describe optical excitations in solids, electrical conductivity and mechanical properties. The single-particle approximation still considers electron-electron interactions, but in an average way so that this is called the mean-field approximation of the electron-electron interactions. In this way, each electron experiences the same average potential \( V(\mathbf{r}) \).

In a crystal lattice, where its main characteristic is its periodicity, the potential satisfies the condition:

\[ V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r}) \]

where \( \mathbf{R}_n \) is any lattice vector. In this case the single-particle Schrödinger equation for an electron in a periodic potential, can be written as:

\[ \mathcal{H}\Psi(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \]

Thus, the problem is distilled down to attaining the correct potential \( V(\mathbf{r}) \) and since the solutions we are interested in in this case are with regard to a periodic crystal lattice, the potential will depend on the geometric characteristics and symmetries of the lattice. Then, our final task is to solve the Schrödinger equation to find the wave function \( \Psi(\mathbf{r}) \).

Furthermore, an important result of the lattice periodicity, is Bloch’s theorem, which states that the wave function \( \Psi(\mathbf{r}) \) can be written as:

\[ \Psi(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n}\Psi(\mathbf{r}) \]

where \( \mathbf{k} \) is the wave vector.

All this implies a very important result that stems from the lattice periodicity: that solving the equation inside a basic lattice unit, we essentially obtain the solutions for the whole of the lattice. Thus, we may obtain the full information about the band structure. This basic unit is the Brillouin zone (BZ) and is defined in reciprocal space. The center of the BZ is termed the \( \Gamma \)-point, as can been seen
in Fig. 2.4 for the diamond cubic and hexagonal diamond BZs, along with other high-symmetry points. For the diamond cubic reciprocal lattice, the three most important high-symmetry points are the X-, K- and L-points, which lie on the \{100\}, \{110\}, and \{111\} surfaces of the BZ, respectively. While for the hexagonal diamond reciprocal lattice important high-symmetry points are the A- and M-points, which lie on the \{0001\} and \{11̅00\} surfaces of the BZ, respectively.

![Figure 2.4. First Brillouin zone (BZ) of the diamond cubic crystal structure. Adapted from Ref.30; (b) first BZ of the hexagonal diamond crystal structure. Adapted from Ref.31. Note that the [111] direction in the cubic system is by definition equal to the [0001] in the hexagonal and both are parallel to the \(k_z\) axis here. This stems from the way the Miller and Miller-Bravais indices are defined and the accepted convention of their notation.](image)

A few words now to explain the correspondence between the high symmetry points of the two structures. The local atomic arrangement of the two crystal structures is very similar. The difference between them is probably best understood by considering the BZs of the crystals as ordered along the [111]/[0001] direction (Fig. 2.4). Along this direction, the atomic layers are stacked on top of one another (Fig. 2.3). As we saw earlier (Ch. 2.1.1 and 2.1.2), for the case of diamond cubic the layers are stacked in an ABCABC... fashion, while in the diamond hexagonal the layers are stacked in an ABABAB... fashion. Both structures present a tetrahedral symmetry, which means that the first and second nearest neighbor the distances are preserved. These structural similarities suggest that the local electronic environments will be similar in both crystals. The cubic diamond structure has two atoms in its unit cell, while the hexagonal diamond has four in its own one. The hexagonal structure has therefore twice as many bands as the cubic one and consequently there is a 2:1 mapping between their respective BZs.\(^{32}\) Due to these similarities, many of the high-symmetry points in the BZs of the two structures have a correspondence between them (known as folding).\(^{32,33}\) What this means is that two points of the diamond cubic BZ are folded (correspond) to one point of the hexagonal
diamond BZ. For example, the \( \Gamma \)- and L-point of the cubic BZ are folded onto the \( \Gamma \)-point of the hexagonal one. So, the band gap of the \( \Gamma \)-point (zone center) of the hexagonal structure can be predicted from the cubic \( \Gamma \)- and L-point. This means that a diamond cubic material with a conduction band minimum at the L-point (lower than at the \( \Gamma \)-point) could be expected to have a direct band gap in its hexagonal diamond polytype. Similarly, the X-point and L-point of the cubic are folded onto a point on the U-line in the hexagonal, which lies 2/3 away from the hexagonal M-point.

### 2.2.1 Methods to calculate the band structure

The two basic methods utilized to calculate the band structure are the empirical pseudopotential method and density functional theory (DFT).

#### 2.2.1.1 Empirical Pseudopotential

The atomic electrons can be roughly divided into two groups: the high-energy state outer or valence electrons and the low energy state inner or core electrons. The valence electrons are the ones that take part in bonds with other atoms while the inner ones are closer to the nucleus. Thus, the wave function can be considered as consisting of a wave function of the valence electrons and a wave function of the core electrons. The empirical pseudopotential method is based on the following assumption: away from the core the wave function may be approximated by the wave function of the valence electrons only and can be used to calculate the properties that depend on the valence electrons only. In this way, the real potential needed, can be approximated by a pseudopotential for the valence electrons only.

#### 2.2.1.2 Density Functional Theory

In density functional theory (DFT) the basic idea is that instead of dealing with the many-body Schrödinger equation, which involves the many-body wave function \( \Psi(\{R_j, r_i\}) \), we deal with a formulation of the problem that involves the total density of electrons \( n(r) \). Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. So, in DFT the dependence on the true potential is replaced by the dependence on the electron density. In this way, the electron density is the variable for the calculation of the total energy of the system using the Hohenberg-Kohn energy functionals. The energy functional for a given density provides the upper limit of the ground state energy of the system based on the variational principle. By
minimizing the energy functional, the ground state electron density can be obtained. The local-density approximation (LDA) is further introduced in order to include the electron-electron interactions. DFT has been very popular for calculations in solid-state physics, although one drawback is that this method is well known to overestimate the band gap by about 2.9%.

2.2.2 Band Structure of Diamond Cubic Silicon and Germanium

As discussed previously in Ch. 2.2, by extrapolating our results from the first BZ, we can characterize the entire crystal’s optical properties. We also discussed that these are summed up in the band structure of the crystal. A typical optoelectronic material with a good optical efficiency is the group III-V semiconductor GaAs (Fig. 2.5a). The Γ-minimum at the conduction band is the global minimum; this means that the transition of charge carriers between it and the top of the valence band is more likely to happen (than in an indirect band gap semiconductor). The transition may take place by a photon of enough energy to

![Figure 2.5. Electronic band structure (a) of GaAs, (b) Si and (c) Ge with the cubic crystal structure; (a) GaAs, a typical efficient optoelectronic material that belongs to the group III-V of semiconductors has a clear direct band gap as is witnessed from the conduction band minimum at the Γ-point; (b) Si has a conduction band minimum at the X-point, which imparts a decisive indirect nature to its band gap; (c) Ge has a conduction band minimum at the L-point, so a charge carrier would need phonon assistance to transition between this point and the top of the valence band, making it an indirect band gap semiconductor. Since it’s so close with the conduction band minimum at the Γ-point, Ge barely misses out on being a direct band gap semiconductor. Adapted from Ref. 34](http://example.com/figure2.5)


excite an electron from the top of the valence band to the bottom of the conduction band. The opposite, is by the recombination of an electron from the bottom of the conduction band with a hole from the top of the valence band with a subsequent release of energy in the form of a photon. The fact that this transition is more likely to happen in a direct band gap semiconductor than in an indirect band gap semiconductor is because in this case phonon assistance in not required for the transition to take place. In contrast, as we can see in Fig. 2.5b, the conduction band at the Γ-point for Si is higher than at the X-point. A transition from the top of the valence band to the X-point needs the assistance of a phonon, making this transition more unlikely to happen (than for a direct band gap semiconductor). Since the absorption or emission of a photon must occur with the simultaneous absorption or emission of a phonon, indirect band gap semiconductors have a low efficiency in the absorption or emission of photons. This results in that light-emitting diodes (LEDs) are chiefly made of direct band gap materials. Ge barely misses out on being direct gap (Fig. 2.5c), in that the L-minimum at the conduction band is very close to the Γ-minimum.

2.2.3 Band Structure of Hexagonal Silicon and Germanium

From rather early on\textsuperscript{34,35}, the nature of the band gap of diamond cubic Si and Ge had been studied and accepted to be indirect; thusly various methods to overcome it have been proposed as was mentioned in section 1.1.2. An interesting approach has been to calculate the band structure of these semiconductors if they were to exist in other crystal systems. Theoretical predictions\textsuperscript{33,36,37} using the empirical pseudopotential method in some cases and DFT within the LDA in others, expect that the band structure picture of Si and Ge changes quite interestingly if they are crystallized in the hexagonal crystal structure. Fig. 2.6a shows the expected band structure of hexagonal Si as elaborated by the pseudopotential method. Even though it still remains an indirect band gap semiconductor, it shows some differences with the picture for the diamond cubic structure band diagram. First, we can already predict from cubic Si (Fig. 2.5b) that hexagonal Si should remain an indirect band gap semiconductor because, as mentioned earlier, the L-point which will fold over to the Γ-point is at the same time higher than the X-point. This we can see in Fig. 2.6a in that the valence band minimum of hexagonal Si is found at the M-point at 0.8 eV, while the gap at the Γ-point is at 1.48 eV. More interesting is the picture for hexagonal Ge. Again, we can already predict from cubic Ge (Fig. 2.5c) that hexagonal Ge should be a direct band gap semiconductor, because the valence band minimum at the L-point folds over to the Γ-point. And, as expected, in Fig. 2.6b, hexagonal Ge is predicted to have a direct band gap of 0.31 eV which is equal to about 4 μm wavelength. The conduction band minimum has a Γ\textsubscript{8} symmetry, while the valence band maximum has a Γ\textsubscript{9} symmetry.\textsuperscript{33} For light
polarized perpendicular \( E_\perp \) to the \( c \) axis of the hexagonal structure the optical selection rules allow a direct transition between them.

**Figure 2.6.** Predicted band structure of the hexagonal diamond crystal structure of (a) Si and (b) Ge, using the pseudopotential method. Adapted from Ref.33

### 2.2.4 Band Structure of Hexagonal Silicon-Germanium

Hexagonal SiGe, being an alloy, will not have a precise stoichiometry everywhere on the nanoscale, meaning that local fluctuations in the ratio of Si:Ge atoms, are expected. Of course, on a larger scale the average ratio is expected to be constant. This issue complicates predictions for the band structure of a hexagonal SiGe alloy, possibly explaining why no significant predictions have been published thus far. Of course, the assumption of a so-called “digital alloy” where e.g. every layer consists of either Si or Ge atoms and with no local fluctuations, simplifies calculations, but this digital stacking is a theoretical concept and is not expected to be realized for the experimentally. Furthermore, a hexagonal SiGe digital alloy case is the case where the only available stoichiometry is half Ge and half Si, i.e. \( \text{Si}_{0.5}\text{Ge}_{0.5} \).

In Fig. 2.7, we show a first approximation to what the band structure of hexagonal SiGe would approximately look like. Essentially we utilized as inputs the values for the minima of the different bands for hexagonal Si and Ge\(^{33}\), which we placed on the left and right vertical axis respectively. Then we connected these points with straight lines. Based on Vegard’s law, in binary semiconducting systems and alloys, the band gap is approximately a linear function of the lattice parameter. Consequently, there exists a linear relationship between the band gap and the alloy composition. In reality, the linear interpolation between the band gap energies is not accurate enough, and a term is added to account for the curvature of the band gap energies as a function of composition. This curvature
correction is known as the bowing parameter. Judging from the bowing parameter of cubic SiGe, this should be a small deviation also for hexagonal SiGe due to folding arguments. The results point to hexagonal SiGe having a direct band gap for about $Si_{0.35}Ge_{0.65}$, where the $\Gamma$-minimum dives below the M-minimum. The value of the band gap is seen to lie around 0.7 eV that is equal to 1.7 $\mu m$, a very close match to the crucial telecom wavelength of 1.55 $\mu m$.

### 2.3 Thin Film Deposition

A thin film is a layer of material that ranges in thickness from a few Å to several $\mu m$. The controlled synthesis or growth of a thin film is known as thin-film deposition and the structure upon which the thin film is deposited is known as the substrate. Furthermore, if the substrate is crystalline then epitaxial deposition may occur when the atomic arrangement in the thin film continues the crystalline structure of the substrate. There are two basic categories of deposition techniques: chemical deposition and physical deposition.

#### 2.3.1 Chemical Deposition

In chemical deposition, a precursor undergoes a chemical reaction at an interface, which results in thin-film deposition. Thin films produced by chemical deposition are usually conformal (as opposed to directional), in that the films...
have thicknesses that are roughly constant over the whole surface area. There are some notable exceptions to this rule that may occur under some conditions, for example when we are dealing with more 3-D like structures, like trenches. A characteristic deposition technique is chemical vapor deposition (CVD), which will be discussed further in Ch. 3.2, as it is the fundamental growth technique utilized in this thesis.

2.3.2 Physical Deposition

In physical deposition, mechanical, electromechanical and thermodynamic methods are used in order to induce particles from the deposition source material to escape its surface. This takes place in a vacuum chamber that allows the particles to have large mean free paths until they arrive at a relatively cooler surface on which they contribute to thin film growth. The large mean free path means that the particles travel in a rather free and straight path, so the films that are deposited are directional rather than conformal. Notable examples are: thermal evaporation, molecular beam epitaxy (MBE) and electron beam evaporation (which we used to deposit Au nanoparticles on NW sidewalls for branch growth – see Ch. 7).

2.3.3 Epitaxial Growth

Epitaxial growth is defined as growth of a single crystal that exhibits a particular crystal orientation and symmetry, determined by the single crystal substrate\textsuperscript{39}. A narrower definition, more in line with this thesis, is that it occurs when the deposited film adopts the same crystalline structure and symmetry that the substrate possesses\textsuperscript{39}. The term stems from the Greek “ἐπιτάξις” (epitaxis), which stems from the roots “ἐπί” (epi), meaning “on” or “on to”, and “τάξις” (taxis), meaning “order”, and thus is transliterated as “order on to”. Two further distinctions can be made: homoepitaxy and heteroepitaxy. Homoepitaxy refers to the case where the epitaxially deposited film is of the same material as the substrate, while heteroepitaxy refers to the rather interesting case where the epitaxially deposited film is of a different material than the substrate. This case is central to this thesis, as this property will be utilized to fabricate hexagonal Si, Ge and SiGe from a template hexagonal substrate, as we will discuss in more detail in the upcoming chapters. A crucial issue in the case of heteroepitaxy is the issue of whether the two materials exhibit the same lattice parameters, or if they differ from each other. If they do differ, there is a lattice mismatch that is defined as:

\[ f = \frac{a_s - a_e}{a_s} \]
where \( a_s \) is the relaxed lattice constant of the substrate and \( a_e \) is the relaxed lattice constant of the epitaxial layer. In this case, the first overgrown layers might accustom themselves to the lattice parameters of the substrate, meaning that the unit cells of the overlayer will deform in order to adjust. This is called pseudomorphic growth. This is accompanied by a build-up of strain energy and the more layers are overgrown, the more strain energy is accumulated. Logically, this strain can be either compressive or tensile, depending on the lattice parameters of the materials. At some point when the overlayers are one too many, resulting in too much strain energy accumulated, the system will try to relieve this superfluous energy by forming crystal defects. Characteristic defects witnessed in these cases are misfit dislocations. A misfit dislocation is a defect where an extra half-plane of atoms is introduced mid-way through the crystal, distorting nearby planes of atoms. These dislocations are detrimental on properties such as the optical, so they are very much unwanted. As we will see further on there are several ways that can be used to grow defect-free structures, up to a certain extent.

### 2.3.4 Modes of Thin Film Growth

During growth of a thin film, the forces that come into play determine the mode of the growth, \textit{i.e.} whether the thin film will form a continuous film on the substrate, whether it will “clump” up to form individual islands, or, in the intermediate case, whether it will form a number of contiguous layers and then transition into subsequent island growth. The driving forces behind this are the interface energies between the substrate, film and vacuum. In a somewhat simple analogy, this can be equated to the conditions that govern the wetting of a surface by a liquid.

![Figure 2.8. Simplified model of an island of a deposited film; \( \gamma_S \), \( \gamma_F \) and \( \gamma_{S/F} \) are the interface energies between substrate-vacuum, film-vacuum and substrate-film, respectively. Adapted from Ref.39](image-url)
In Fig. 2.8, if $\gamma_S$ is the interface energy between the solid substrate and vacuum, $\gamma_F$ the film-vacuum interface energy, $\gamma_{S/F}$ the film-substrate interface energy and $\phi$ the contact angle, then we have:

$$\gamma_S = \gamma_{S/F} + \gamma_F \cos \phi \quad \text{(Young's equation)}$$

2.3.4.1 Frank – van-der-Merwe/Layer-by-layer growth

In the Frank – van-der-Merwe (FM) growth mode (see Fig. 2.9a) the interaction between substrate and layer atoms is stronger than the interaction between the layer atoms themselves. This is the case where the film lowers the surface energy and has a small lattice mismatch with the substrate (Fig. 2.10). Thus it tends to spread across the substrate surface, resulting in smooth layer growth\(^{39}\). The consequence is that the contact angle $\phi = 0^\circ$, which in turn means that from Young’s equation:

$$\gamma_S \geq \gamma_{S/F} + \gamma_F$$

Furthermore, Young’s equation, in the case of FM growth, can be expanded to:

$$\gamma_S \geq \gamma_{S/F} + \gamma_F + C \kappa t \ln \left(\frac{p_0}{p}\right)$$

where $\zeta = p/p_0$ is the degree of supersaturation, $p_0$ is the equilibrium vapor pressure of the gas phase above the deposited film, $p$ is the pressure and $\kappa$ is a constant. From this, we can see that the growth mode of a certain material on a substrate is not a constant material parameter, but that the growth mode can be changed by varying the supersaturation conditions. For example, for

\[\text{Figure 2.9. Modes of thin film growth.} \ \Theta \text{ is the surface coverage in monolayers (ML).} \]

(a) Frank - van-der-Merwe or layer-by-layer growth; (b) Stranski - Krastanov or layer-plus-island growth; (c) Volmer - Weber or island growth. Adapted from Ref.\(^{39}\)
heteroepitaxial growth with small lattice mismatches, \textit{i.e.} small difference in the lattice constants of the two materials, FM growth will be favored for increasing supersaturation.

### 2.3.4.2 Volmer – Weber/Island growth

In the Volmer – Weber (VW) growth mode (see Fig. 2.9c) the interaction between the layer atoms themselves is stronger than the interaction between the substrate and layer atoms. This is the case where the film increases the surface energy and may or may not have a lattice mismatch with the substrate (Fig. 2.10). Thus, there is a tendency to minimize the surface covered, resulting in growth of only islands. The consequence is that the contact angle $\phi > 0^\circ$, which in turn means that from Young's equation:

$$\gamma_S < \gamma_{S/F} + \gamma_F$$

Also in this case, Young's equation can be expanded to:

$$\gamma_S < \gamma_{S/F} + \gamma_F + Ckt \ln\left(\frac{p_0}{p}\right)$$

\textbf{Figure 2.10.} Regions of misfit strain and surface energy in which different growth modes are observed. At small misfit strains, a film that lowers the energy of the surface produces smooth layer-by-layer (FM) growth. When the surface energy is raised by the film or when the strain energy is too large, the growth is three-dimensional.
So, for example, for heteroepitaxial growth VW growth will be favored for decreasing supersaturation. Also, in case of heteroepitaxial growth with a large lattice mismatch, not even a few smooth layers will grow as in SK mode (see below), but rather just islands, because the lattice of the adsorbate is so different than the substrate that it is almost impossible for the adsorbate to accommodate so high strain.

2.3.4.3 Stranski – Krastanov/Layer-plus-island growth

In the Stranski – Krastanov (SK) growth mode (see Fig. 2.9b) we observe growth of a number of smooth layers with subsequent transition to growth of islands of the adsorbate material on top of the layers. In this case, the lattice mismatch also has an effect due to an increase in strain energy (Fig. 2.10). Practically, even if the film decreases the surface energy as in FM growth, the accumulation of strain energy makes island growth favorable after a critical thickness.

In summary, all of the mentioned growth modes can be observed in Fig. 2.10, where they are related with the surface energy change and misfit strain. For a low surface energy and small misfit strain, FM growth mode is favored, while for a low surface energy and high misfit strain, SK growth mode is favored. For high surface energy VW growth mode is favored, irrespective of misfit strain.

2.4 Nanowires

Nanowire (NW) growth and study has in recent years developed in a fertile scientific field evidenced by the large number of publications and interest and with a multitude of important discoveries and breakthroughs\textsuperscript{40}. NWs and the vapor-liquid-solid (VLS) growth mechanism -which is a mechanism by which NWs grow- were discovered by Wagner and Ellis at Bell labs when they observed growth of Si NWs which they published in their famous 1964 paper\textsuperscript{41}. The VLS mechanism of NW growth has since been observed even in lunar rocks\textsuperscript{42} brought back from the NASA Apollo missions and on meteorites, making this a fundamental growth mechanism in nature\textsuperscript{43}, not only evidenced in the lab.

2.4.1 Vapor-Liquid-Solid Growth Mechanism

The VLS growth mechanism is a bottom-up method for fabricating NWs and involves, as the name suggests, three material phases; the vapor phase, the liquid and the solid. The vapor phase refers to the volume of precursor gasses used in this process and that surrounds the growing NW, the liquid refers to a liquid catalyst that is present that acts to catalyze growth and the solid refers to the
solid NW that is growing. CVD is the main technique in which the VLS mechanism is utilized to grow high quality NWs.

When precursor gasses \textit{(vapor)} are injected into the CVD growth chamber, they thermally decompose \textit{(pyrolyze)} to their constituent elements. This takes place at relatively high temperatures. At lower temperatures decomposition takes place with the help of the catalytic action of the catalyst particle and/or due to dangling bonds on the substrate surface. When the chamber is heated, the catalyst particle (Fig. 2.11a) situated on a substrate \textit{(solid)} forms a eutectic alloy droplet \textit{(liquid)} with the precursor (Fig. 2.11b). For example, in the case of Si NW growth mediated by Au catalyst particles, the Au-Si eutectic alloy system has a eutectic temperature of 363 °C at 18.6 atomic % Si. The droplet proceeds to supersaturation conditions, at which point nucleation at the droplet - substrate interface is favored. This nucleation process results in the growth of a full layer at the interface after which the liquid droplet is “pushed” upwards while an additional layer is nucleated at the new interface. This continues and finally produces a NW crystal directly below the droplet (Fig. 2.11c).

![Figure 2.11. NW growth via the VLS mechanism. In this case the catalyst particle is Au. (a) Solid Au particle on the substrate surface; (b) eutectic alloy formed with precursors after temperature increase; (c) precursor supersaturate the eutectic commencing NW growth; (d) the NW grows to the desired length with time. Adapted from Ref. 45](image)

In our case, Au was utilized as a catalyst particle. It is the material of choice for Si NW growth\textsuperscript{44} because it possesses a eutectic point at a low temperature and high Si solubility, has a low vapor pressure at elevated temperatures meaning that it will not evaporate easily, the Au-Si alloy has a high enough surface tension that contributes to a stable nanowire-droplet system. Finally, Au is easily available, nontoxic and chemically inert.

As mentioned previously, precursors can decompose to adatoms by thermal decomposition \textit{(pyrolysis)}, the catalytic effect of the catalyst particle and by dangling bonds. These paths to decomposition can be affected by the tuning of growth parameters. For example, at low temperature, decomposition takes place
mainly at the catalyst particle, while pyrolysis and surface decomposition are suppressed. This will result in VLS NW growth. On the other hand, if the growth is carried out at higher temperature, pyrolysis and surface decomposition can start to play a more active role. Resulting in thin film growth around the NW at the same time as the VLS NW itself is growing. In this case a tapered NW will be obtained. Finally, if no catalyst is present, decomposition will take place due to pyrolysis and by dangling bonds.

A critical difference between standard thin film layer growth and NW growth is the involvement of the catalyst particle. The catalyst particle may drastically reduce the temperature of NW growth as compared to classic thin film layer deposition. For example disilane (Si$_2$H$_6$) decomposes to deposit amorphous layers at 640°C for standard thin film growth$^{46}$, while Si NW growth by the VLS mechanism with Au catalyst particles starts at temperatures as low as 363°C$^{47}$.

2.4.2 Nanowire Heterostructures

Nanowire-based heterostructures can enhance the functionality of the system. By modulating the doping within one material and/or composition with different materials, we can achieve surface passivation, fabrication of p-n junctions, and crystal structure transfer, all the while providing us with an added degree of freedom of design of nanostructures. The optical properties of

![Figure 2.12. Nanowire heterostructure synthesis. (a) Preferential reactant incorporation at the catalyst (growth end) leads to one-dimensional axial growth. (b) A change in the growth parameters leads to either (c) axial heterostructure growth or (d) radial heterostructure growth depending on whether the reactant is preferentially incorporated (c) at the catalyst or (d) uniformly on the wire surface. Alternating reactants will produce (e) axial superlattices or (f) core-multi-shell structures. Adapted from Ref.$^{48}$](image)
nanowires may be degraded by the presence of dangling bonds at the nanowire surface that will act as recombination centers for charge carriers, but with the in-situ overgrowth of a passivation layer without the formation of a grain boundary, this can be overcome. Also, p–n junctions which are the elementary "building blocks" of most semiconductor electronic devices such as diodes, transistors, solar cells, LEDs, and integrated circuits, can be fabricated simply by an in-situ change of doping during growth. Furthermore, and more central to this study, NW heterostructures enable us to grow epitaxial crystals that adopt the crystal structure of the substrate. The two main types of NW heterostructures (see Fig. 2.12) are axial and radial and will be scrutinized in the two following sections.

2.4.2.1 Axial Nanowire Heterostructures

With the use of NWs it has been possible to fabricate a wealth of heterostructures. By turning on and off various precursor gas flows, we can affect the species that are supersaturated in the droplet, resulting in a tuning of the NW composition and/or doping in the axial direction and which are known as axial NW heterostructures (Figs. 2.12c and 2.12e). Many examples exist for various material systems; Si-Ge\textsuperscript{49} for group-IV, InAs-InP\textsuperscript{50}, GaAs-GaP\textsuperscript{51} for the III-V group, but also GaP-Si\textsuperscript{52} for the combination of group-IV and III-V's. An example of this can be seen in Fig. 2.13, where we can observe radial NW heterostructures with a base segment of GaP and a to p segment of Si (Fig. 2.13a) and also even more complex NW heterostructures (see Fig. 2.13b) of four consecutive GaP/Si segment. The reason to do this with NWs is that in bulk

![Figure 2.13. Axial NW heterostructures. (a) A GaP/Si axial NW heterostructure. Scale bar 1 \(\mu m\), tilt angle 45°; (b) Even more complex structures can be fabricated with multiple (4 in this case) GaP/Si interfaces. The diameter change at the junction between the first and second GaP/Si segments is due to a change in the droplet contact angle on the GaP and Si surface. Scale bar 500 nm, tilt angle 45°. Adapted from Ref.\textsuperscript{52}](image)
systems, threading dislocations are usually formed at the junction due to a mismatch in lattice constants and thermal expansion coefficients, even for a small lattice mismatch material combinations such as GaP/Si (0.3%). But by utilizing NWs these problems can be solved due to the fact that lattice strain is elastically relieved due to the unique NW geometry.

2.4.2.2 **Radial (Core/Shell) Nanowire Heterostructures**

If, after VLS NW growth, we subsequently alter the growth parameters such as temperature and/or precursor flow, we can assist diffusion-mediated surface growth while suppressing any further VLS growth. This is the case of radial NW heterostructures, where a thin film layer is deposited around a NW substrate essentially like a shell around a NW core. Thus, such heterostructures are more commonly referenced in literature as core/shell NWs (see Figs. 2.12d, 2.12f and Fig. 2.14). In general, VLS is initiated at lower temperatures compared to thin film growth, due to the catalytic effect of the catalyst particle. So, by using an increased temperature thin film growth is favored.

![Figure 2.14](image-url) **Figure 2.14.** Core/shell NW heterostructures. (a) GaP/Si core/shell NW and (b) the corresponding radial compositional profile, as determined using STEM-EDX; (c) GaP/Si/SiGe core/multishell NW and (d) the corresponding HAADF intensity profile.
Chapter 3 – Experimental Methods and Techniques

In this chapter, the experimental setups and techniques employed to grow and characterize NWs and NW heterostructures will be discussed. Initially, wafer preparation is needed in order to pattern it with the catalyst particles necessary for the VLS NW growth as well as cleaning of the surface. Then, the growth takes place in a MOVPE reactor. The grown samples are initially characterized by SEM, while a more in-depth characterization is done with the help of TEM. The crystal structure and phase purity is further assessed by TEM and XRD measurements. The mechanical and high-pressure stability is probed by Raman measurements; it also completes the TEM and XRD observations on the crystal structure type and quality.

3.1 Substrate Patterning

Nanoimprint lithography, colloid deposition and annealing of continuous thin metal films were employed to create and/or deposit catalyst particles, intended for VLS growth, on the desired substrate surface.

3.1.1 Nanoimprint Lithography

Nanoimprint lithography is utilized to pattern a regular array of catalyst particles -intended for VLS growth- with a predefined size, position and distance between them, over a whole substrate wafer with the accuracy of nanoscale resolution. This method is perhaps not the most flexible in terms of the geometric characteristics of the array, because it involves the use of a master patterning mask, but it more than compensates in that it offers us balance between being fast and the production of a regular array over a whole wafer. Resulting benefits are the ability to show that the experimental results are reproducible over a whole wafer -if so desired- and that any further characterization, be that TEM, XRD, Raman spectroscopy, optical measurements, yields confident results due to the high number of NWs. As an example, XRD, in which the detected signals depend on the scattering volume of the sample, yields much clearer and transparent results when analyzing a sample with so many NWs stemming from catalyst particles deposited by the nanoimprint technique.

Before starting the procedure of creating the array on the substrate, a stamp has to be created. The stamp has to be flexible and thus the ability to be used many times. The stamp has to be inscribed with the geometric features of the array that are to be imprinted finally on the substrate; this is achieved by the use
of a Si wafer with a master pattern of arrays of holes fabricated by electron beam lithography (EBL) and which is transferred onto the flexible polydimethylsiloxane (PDMS) stamp. The final result of this process is a flexible stamp with protruding pillars$^{56-58}$.

**Figure 3.1.** Schematic drawing of the nanoimprint lithography process. (a) PMMA and sol-gel resist (TMOS-MTMS) deposited on the substrate; (b) application of PDMS stamp; (c) removal of stamp; (d) etching with CHF$_3$; (e) etching with O$_2$; (f) Au deposition and (g) lift-off with acetone.

The initial step in the fabrication of the catalyst particle array on a substrate, is to coat the substrate wafer with a 300 nm thick layer of low molecular weight polymethylmethacrylate (PMMA) by spin-coating and subsequent baking at 150°C for 15 min. Secondly, a layer of sol-gel imprint resist of tetramethoxyorthosilicate (TMOS) and methyltrimethoxysilane (MTMS) is spin-coated onto the PMMA$^{59}$ (see Fig. 3.1a). Within 1 min of this, where the sol-gel is still liquid, the PDMS stamp is applied and the features of the stamp (see Fig.
3.1b) are filled with the sol-gel resist due to capillary action. The sol-gel is then left to form a silica glass, which takes place at about $2 - 3 \text{h}$. At this point it is safe to remove the flexible PDMS stamp by careful and slow peeling and we are left with an array of holes on the sol-gel (see Fig. 3.1c).

![Figure 3.2](image)

**Figure 3.2.** Nanoimprint lithography and growth. (a) SEM image of a nanoimprint array of Au particles on GaP substrate. Note the strict geometric characteristics of the array, namely constant distances (pitch) between the Au particles which reside in an array of square symmetry; (b) Close-up view of (a). Note the constant pitch of 500 nm; (c) SEM image of GaP/Si core/shell heterostructure NWs grown from the array in (a). The advantage this method is evident in that it provides a vast number of uniform NWs.

The superfluous sol-gel that is at the bottom of the holes is removed by reactive ion etching (RIE) with fluoroform ($\text{CHF}_3$) for 40 s (Fig. 3.1d). Of course, the top of the pillars is also etched, but as is understandable, when the sol-gel at the bottom of the holes has been etched, there still remain sol-gel pillars due to their height. The underlying PMMA that is under the pits is etched by RIE with $\text{O}_2$. This etching is done in order to provide access to the substrate underneath. A slight over-etch is performed in order to remove any residual PMMA, resulting in a slightly larger diameter at the bottom of the final etch pits (Fig. 3.1e). The next processing step is to evaporate gold (Au) in an evaporator and create an Au layer (Fig. 3.1f). The thickness of the layer and the hole diameter provide us consequently with control over the final particle diameters, *e.g.* an 8 nm thick Au
layer provided us with final droplets of $90 - 100 \text{ nm}$, while a $2 \text{ nm}$ thick Au layer provided us with approximately $50 \text{ nm}$ droplet diameters. The final step is the so-called lift-off, where the PMMA is removed by acetone [(CH$_3$)$_2$CO], which results in the total removal of the PMMA/Sol-gel/Au pillars. After this, we finally obtain a full wafer completely covered with the desired array of catalyst particles (Fig. 3.1g). In Figs. 3.2a and 3.2b, SEM images is shown of the end product of the nanoimprint lithography process; Au particles deposited on the substrate with the distinctive uniformity of the array produced. In Fig. 3.2c the uniform NW array fabricated from the nanoimprint Au particles is shown; note the Au particles on top of the as-grown NWs.

### 3.1.2 Colloid Nanoparticle Deposition

Colloid nanoparticle deposition is a technique for depositing catalyst particles intended for VLS growth. In a colloid, the solid catalyst nanoparticles are suspended in a liquid, and the colloid is deposited (in our case by spin coating) on the substrate. It is utilized to pattern a substrate with a high density and a predefined diameter (see Fig. 3.3), but is much more random than nanoimprint. It offers us faster deposition times than nanoimprint coupled with catalyst particle diameter control. This can be for example a fast method to do several initial experiments, with a number of samples with different diameters at the same time, in order to discover relatively good growth conditions, before moving to optimization for the nanoimprint technique. The colloidal dispersions obtained from the manufacturer each contain metal nanoparticles with a narrow size distribution, the average diameters ranging from $2 \text{ nm}$ up to $150 \text{ nm}$, depending on the dispersion. The Au nanoparticles are capped with an organic shell and are suspended in H$_2$O. Deposition is performed by spin-coating and subsequent drying of any excess H$_2$O by N$_2$. An annealing step is required once

![Figure 3.3](image_url)
the sample is placed in the growth chamber in order to remove the organic cap and facilitate some absorption of the substrate material into the colloid. In this thesis Au colloids were utilized for the subsequent VLS growth of NWs.

3.1.3 Catalyst Particle Creation by Annealing

In this method, a thin film of the material to be used as catalyst particles is deposited on the substrate and consequently annealed to produce particles. During the annealing, dewetting takes place, which results in balling-up of the metal into particles that are spread on the substrate surface. This method is also fast, but gives less control over the particle diameter than the other two techniques described in Ch. 3.1.1 and 3.1.2. The diameter of the particles can be controlled, to some extent, by the thickness of the deposited layer. Experimental conditions have to be optimized, i.e. annealing temperature, annealing time, layer thickness, in order to produces more or less the desire outcome. Several phenomena come into play, such as dewetting of the film to produce the droplets, the type of substrate surface or Ostwald ripening, where larger droplets grow even bigger by “consuming” smaller ones. An advantage of this technique compared to colloid deposition and to nanoimprint, is that it results in a pure Au layer as we avoid the possibility of contamination by organic compounds from the colloid nanoparticle capping or residues from the resist, respectively. Another benefit of this technique, compared to colloid deposition, is that we can partially control where the particles are deposited e.g. when the goal is to deposit particles on the sidewall of the NWs, in order to grow VLS NWs out of the sidewalls, in a way that resembles branches on a tree trunk. In this case, the layer deposition can take place under an angle, i.e. the flux of deposition material will be aimed at an angle with respect to the NW sidewalls. In this way, the NWs will “shadow” the substrate, meaning that the net layer deposition will take place on the NW sidewalls, rather than on the substrate. On the contrary, if colloids where to be used for this process, it would result in particles covering all over the NW sidewalls and on the substrate, which could result in unwanted NW growth on the substrate. More on this will be presented in Ch. 7, where growth of NW “branches” on NW “trunks” will be presented.

3.2 Metal-organic Vapor-Phase Epitaxy

Metal-organic vapor phase epitaxy (MOVPE) is a type of chemical deposition technique well-suited for epitaxial crystal growth. This technique is widely used by the industry to create high quality single-crystalline thin films with a plethora of materials on a wide variety of substrates. Metalorganic (MO) as well as hydride precursors are used. In Fig. 3.4 a schematic drawing of the typical layout
of an MOVPE reactor is provided. The MO precursors are made up by a metal atom and an organic group and are kept in bubblers that provide a stable environment (temperature consistency). As an example of MO precursors, we mention tri-methyl-gallium (TMGa) that is a precursor for gallium (Ga). A carrier gas is needed to draw material from the bubblers and push it to the main reactor growth chamber. This carrier gas is $\text{H}_2$. On the other hand, the hydrides are kept in gas bottles and are usually already in the form of a mixture of the pure precursor and $\text{H}_2$. Examples of hydride precursors are disilane that is a precursor for Si, germane ($\text{GeH}_4$) that is a precursor for Ge and phosphine ($\text{PH}_3$) that is a precursor for phosphorus (P). Given the fact that many of these gasses (e.g. $\text{PH}_3$) are highly toxic, these gas bottles are usually kept in isolated and secure cabinets (e.g. in the subfab, which is the area underneath a semiconductor fabrication –or fab– plant), in order to minimize exposure risk. In the case of the hydrides, the gas flow (concentration of growth-contributing units) that is injected into the reactor is regulated at the source, while in the case of the MOs, the gas flows are regulated by a series of highly accurate mass-flow controllers. In both cases we are able to get a wide range of partial pressures per precursor, giving us more stoichiometric and growth opportunities.

Figure 3.4. MOVPE reactor schematic. Adapted from Ref. 45

The place where the growth and deposition takes place is the reactor chamber. Its main features are: an inlet for the mixture of the precursor/$\text{H}_2$ gasses, a susceptor where the substrate is placed, heating elements and an exhaust. In our case, we utilize a cold-wall low-pressure (50 mbar) Aixtron Close Coupled Showerhead (CCS) reactor. The inlet of the precursor gasses is at the top of the chamber (vertical geometry), so that the gasses are directed in a downward fashion, and consists of many small water-cooled inlet holes (showerhead), in order to provide a more homogenous precursor distribution. Another contributing factor to the homogeneity is that the whole reactor
geometry and design of the inlets serve the purpose of avoiding any turbulent flows as the gasses reach the substrate.

The susceptor is made of radiation-absorbing graphite and is the place where the substrate is placed; it rotates at a set rotation frequency and has a shape that further helps the precursor to arrive in a homogenous fashion at the growth interface and subsequently flow away to the exhaust. Fig. 3.5a shows a schematic drawing of the susceptor and shows the vertical geometry used in the experiments presented in this thesis. The close spatial proximity (16 mm) of the showerhead and the susceptor provide us with the ability to switch fast between different precursors, which e.g. helps us achieve abrupt heterostructure junctions. Fig. 3.5b shows the actual susceptor and showerhead of the MOVPE reactor used for the experiments presented in this thesis; their close proximity is visible.

![Figure 3.5](image-url)

**Figure 3.5.** (a) Schematic of the susceptor; (b) image of the MOVPE reactor that was used for the growth of the structures presented in this thesis. The top plate with the precursor inlets can be distinguished along with the susceptor and the substrate that awaits deposition. Adapted from Ref.45

Underneath the susceptor are W (tungsten) heating coils through which an electric current is passed that results in Joule heating (resistive heating). This results in infrared (IR) radiation emission, which is absorbed by the graphite susceptor and which consequently heats up. The W heating elements are divided into three separate zones that can be tuned separately to ensure an even temperature distribution over the whole susceptor -and most importantly- wafer surface. Optical sensors mounted at the top of the reactor showerhead allow monitoring of the substrate temperature profile *in-situ*, by measuring black-body radiation. This provides us with feedback and assists us in the further adjustment of the currents that are passed through the W coils of the different heating zones. Thus, we can achieve the desired growth temperature and its uniformity across the susceptor and wafer surface.
As mentioned previously, we utilize a cold-wall reactor, where the lining of the chamber is made of quartz that is largely transparent to radiant IR heating. This means that the walls will be generally quite colder than the susceptor, meaning that little deposition will take place on them. Since mostly the susceptor is heated, any precursor thermal pyrolysis takes place for the most part when the precursors encounter the hot susceptor surface, in order to provide the growth-contributing adatoms.

Once the precursor pyrolysis has taken place at the susceptor, the resulting adatoms diffuse across the substrate surface and bond with its atoms in order to form an epitaxial layer. High-quality crystal growth necessitates high mobility of the adatoms, which can be achieved by e.g. increasing the temperature.

The whole system is under a specified total pressure, which can be controlled. Since the system pressure determines the partial pressure of the precursors, this results in a further control of the precursor concentrations and deposition rates.

The Si, Ge and SiGe thin-films and NWs presented in this thesis have been grown by utilizing Si$_2$H$_6$ and GeH$_4$ precursors. For the GaP NWs, TMGa and PH$_3$ were used, while HCl (hydrogen chloride) was used to prevent undesired NW tapering.

### 3.3 Scanning Electron Microscopy

*Scanning electron microscopy* (SEM) is a type of microscopy that utilizes electrons for imaging. This kind of microscopy has enabled us to achieve an impressive maximum resolution of approximately 1 nm. The SEM improved resolution by two orders of magnitude compared to its predecessor, the optical microscope. Images are obtained by scanning the sample surface with a focused beam of electrons in a raster scan pattern. The interaction between the electrons and the sample atoms results in the production of various signals, which provide information about the sample's surface topography and composition.

The electrons are produced by thermionic emission from an electron gun and accelerated through the SEM column by an accelerating voltage (see Fig. 3.6 for a schematic diagram of the SEM column). Thereafter, an electromagnetic condenser lens focuses the electrons to a very narrow beam, which passes through a scan coil that moves the beam in the $x$- and $y$- directions. This results in a raster scan of the sample surface. During the interaction of the electron beam with the sample, the electrons may lose energy by random scattering and absorption within the interaction volume, whose size depends on the electron energy, the atomic number and density of the sample material. The interaction that takes place between the electrons and the sample atoms produces:

- Secondary electrons (SE) of low energy due to inelastic scattering
Back-scattered electrons (BSE) of high energy due to elastic scattering
Auger electrons
Characteristic X-rays
Other types of electromagnetic radiation, such as cathodoluminescence

Finally, the whole gun column is kept under vacuum, in order to increase the mean free path of the electrons.

Figure 3.6. Schematic diagram of the column of the Zeiss Sigma SEM system, used for image production in this thesis.

The basic way of image production is by using SEs, which originate from the upper few nm below the sample surface, due to their low energy. Even though SEs are generated in the whole interaction volume of the sample with the electron beam, they have a low kinetic energy and are subject to inelastic scattering and energy loss during their passage through the specimen, thus they are strongly attenuated with distance traveled. As a consequence, only SEs from a few nm inside the sample surface can escape and contribute to image generation. This results in a type of imaging that is sensitive to the surface topography with a relatively sufficient depth of field, which means that we get a 3-D like image. An annular SE detector that is positioned within the column collects the signal from the SEs and thus is termed as an in-lens detector. In Fig. 3.7, SEM images of NWs are shown, generated by the SE signal, so the surface topography is visible. The BSEs on the other hand, contribute to the production
of an image that is sensitive to the sample chemical composition, because heavy elements backscatter more than light elements.

The samples need little to no preparation at all before examination, a contributing factor to making SEM a rather quick and handy tool to assess the overall morphology of the NWs.

![Figure 3.7](image)

**Figure 3.7.** SEM micrograph of GaP/Si core/shell heterostructure NWs using the in-lens annular SE detector, which is sensitive to the topography of the sample surface. (a) Overview at 30° tilt angle; (b), (c), (d) and (e) top-view of the NWs at ×20k magnification, ×80k, ×150k and ×500k respectively. Note in (e) that the magnification is sufficient enough to even discern faceting of the Au eutectic particle (left over from the VLS growth of the GaP core NWs).

In this thesis, a Zeiss Sigma SEM was utilized to investigate the NWs and was mainly operated at an accelerating voltage of 10 kV, while an in-lens detector for detecting SEs was used most of the time.

### 3.4 Transmission Electron Microscopy

*Transmission electron microscopy* (TEM) is a type of microscopy that utilizes electrons like SEM, but can achieve an even higher maximum resolution down to about 50 pm (1 pm = 10⁻¹² m). In contrast with SEM, TEM uses a beam that is transmitted *through* the sample and not just scanned across its surface. Thusly it is able to provide us with a sufficient enough resolution to get detailed information on the atomic arrangement – crystal structure – of the samples as well as visualization of any defects present, nano-scale composition and stress. This high resolution can be attributed to the high electron acceleration voltages employed, typically reaching values of up to 300 kV. In this way, the *de Broglie* wavelength of the electrons can be in the order of pm, resulting in *atomic resolution*:

\[ \lambda = \frac{h}{p} \]
where \( h \) is Planck’s constant and \( p \) is the electron momentum, which is proportional to the acceleration voltage. This means that the higher the acceleration voltage is, the smaller the wavelength of the electron is. Finally, the system is kept under vacuum, as the SEM, in order to increase the mean free path of the electrons.

Even though TEM provides the aforementioned plethora of important nano-scale information, as compared to the SEM there are a number of drawbacks. One of the main issues that makes it less convenient, is the fact that it takes much more time to prepare a well-suitied sample, because in order for the beam to travel through it, a thinning of the sample is required. This thinning should result in a sample on the scale of about 100 nm in the direction of the beam. In our case, where we’re dealing with NWs, the radial dimension is already on the required scale size, so no further thinning is required for observation through the side. But for the observation through the axial NW direction, that is the direction along which the NW grows and that can be several \( \mu m \) long, a thinning is essential. Furthermore, the actual sample analysis and probing, lens adjustment and all necessary instrument tuning to achieve good viewing conditions, is more demanding than SEM and adds to the time expenditure.

In Fig. 3.8, a schematic drawing of a TEM is presented. The main part of a TEM system is the column, which can be divided into three components:

- The illumination system
- The objective lens and stage system
- The imaging system

The illumination system comprises the electron gun and the condenser lenses and its role is to extract the electrons from the source and transfer them to the sample. There are two principal modes in which the illumination system may be operated in: parallel beam and convergent beam. The first mode is used primarily for TEM imaging while the second is used mainly for scanning TEM (STEM) imaging, utilizing a convergent beam.

The heart of the TEM beats at the objective lens and stage system. All of the beam and specimen interactions take place here and the two fundamental TEM operations occur; the creation of the various images on one hand and diffraction patterns (DPs) on the other. Subsequently they are magnified for viewing and recording. The objective lens is clearly the most important lens in a TEM because its quality determines the overall quality of all the information about the specimen that we extract. The stage is where the sample is located and allows for the sample to be tilted.

Finally, the imaging system utilizes several lenses to magnify the image or the DP produced by the objective lens and to focus these on a detector. The final lens
can be known as the projector lens, because it projects the final image or DP onto a detector, fluorescent screen etc.

**Figure 3.8.** Schematic representation of a transmission electron microscope (TEM). At the top, the electron gun can be seen. Further down are the various lenses and sample stage. Finally, the image is projected onto a screen or a CCD. Adapted from Ref. 45

A brief description of the main stages from beam generation to acquisition of information will follow. Initially, an electron gun, given high enough voltage, emits electrons by thermionic or field electron emission. The electrons are then accelerated by a voltage of typically $60 - 300 \, kV$. Magnetic fields are consequently employed to provide sufficient control over the beam. This materializes in the various lenses employed. The condenser lenses provide the primary beam formation, meaning control over the beam path as well as the beam itself, *i.e.* to make the beam parallel (conventional TEM) or focused (STEM). Scan coils are utilized to either tilt the beam, so it impinges on the sample under a certain angle, or translate the beam parallel to the optical axis, so the beam interacts with a specific portion of the sample. The beam then interacts with the sample that is situated at the stage, while the objective lens essentially forms the images and DPs. The projector lens expands the beam before it hits a fluorescent
A main advantageous characteristic of the TEM is the possibility to obtain information in real space (imaging mode) and reciprocal space (diffraction mode) almost simultaneously. First of all, the beam interacts with the specimen and after exiting, forms a DP in the back (rear) focal plane (BFP) in diffraction mode. By means of the projection system, the BFP – and thus the DP – can be projected and recorded onto a CCD. Depending on whether the sample is single-crystalline, polycrystalline or amorphous, the DP will be characteristic of that. Furthermore, for a crystalline sample, the DP is a representation of reciprocal space, so distances on the DP correspond to angles of scatter at the specimen. Upon tilting the sample with respect to the electron beam, the diffraction pattern – the projected reciprocal space – will change accordingly.

Concerning crystalline samples, which will be the focus of this thesis, an important matter is to align the sample to a desired zone axis. A zone axis refers to a specific direction within the crystal and is parallel to a crystal vector. Since a given set of planes has a given spacing and symmetry, the planes will diffract the beam in a characteristic way, resulting in a characteristic DP. This is important when we want to align the beam with a specific zone axis, i.e. to image the crystal along a specific crystal direction. Observing the DP and tilting the sample (sample stage) we will at some point record a DP that is characteristic of the zone axis we want and thus we know that the sample is aligned in the desired zone axis (crystal direction). And why would we want to do that? Because it can provide us with a fingerprint of the crystal structure. By combining information on zone axis patterns acquired from different sample orientations allows for a unique identification of the structure of the crystal under study. This is furthermore paramount to the identification of crystal defects, because the identity of the structure may be hidden when observing in the wrong direction and even crystal defects may be totally obscured, leading to wrong conclusions.

In image mode, the beam is allowed to continue its path undisturbed after the BFP and an image is formed at the image plane. So if a detector is placed there, an image will be obtained. Practically, the image plane is further magnified by the projection lenses and afterwards the image is obtained. There are almost forty different imaging modes that a TEM (operated in both conventional TEM and STEM configurations) can implement. The basic imaging modes for conventional TEM and relevant to this thesis are:

- Bright-field TEM (BFTEM). In this case, the bright central spot of the DP is selected by the use of an aperture in the BFP. Thus, the electrons from larger scattered angles are omitted. There are two types of contrast contributions: mass-thickness contrast and diffraction contrast. Mass-thickness contrast is a result of Rutherford scattering of the beam.
electrons by the sample atoms. This means that if the beam encounters a heavy element, electron scattering will occur at larger angles than would occur for atoms of a lighter element. Also, in thicker sample regions, more scattering events take place. The result is that in a BFTEM image, sample regions with heavier elements appear darker, while regions with lighter elements appear brighter and that regions that are thicker appear darker, while regions that are thinner appear brighter. On the other hand, diffraction contrast, which is based on electron diffraction (Bragg diffraction), takes place for parallel planes of atoms in a crystal. Bragg diffraction will occur at larger angles (than the central bright spot of the transmitted beam) when the Bragg condition is met; see next Ch. 3.5. By selecting the central beam, these electrons are omitted, resulting in darker regions in a BFTEM image of crystalline regions. Furthermore, different plane spacings, as would happen for different crystal structures or crystal defects, will diffract at other angles, contributing to diffraction contrast. This has an important consequence; a crystal defect, as is the case for a planar stacking fault (SF), will diffract at another angle, resulting in contrast. Thus, in this kind of imaging mode, SFs can be distinguished.

- **Dark-field TEM (DFTEM).** Almost the complete opposite of BFTEM is true in this kind of imaging mode. From the DP, the central spot is omitted and a secondary spot is selected by an aperture in the BFP. Again, we have mass-thickness and diffraction contrast, but since electrons from larger angles are allowed to pass, diffraction contrast plays a significant role in this case. Given a crystalline sample tilted to the correct zone axis, will result in crystalline regions being brighter (since these regions scatter at larger angles and with the use of the aperture, we have allowed these electrons to pass). So also in this kind of imaging mode SFs can be distinguished. Due to mass-thickness contrast, regions with heavier elements and which are thicker appear bright, while lighter elements and thinner regions appear dark.

- **High resolution TEM (HRTEM),** allows for the highest magnifications with a present record resolution down to 0.5 Å (1 Å = 10^{-1} nm = 10^{-10} m), giving us the capability to observe the atomic structure of the sample. In this case, the direct beam and the scattered ones are selected at the same time by the use of a large aperture. The image is formed by the interference of the diffracted beams with the direct beam, resulting in the generation of fringes. Consequently, this type of contrast is known as phase-contrast. So, the final image is a result of a change in the phase of the electrons, given a crystalline sample that has been tilted to a zone axis, this type of phase-contrast imaging gives us the capability to discern individual columns of atoms and is a powerful tool to identify different crystal structures as well as defects.
At this point it is noteworthy to mention the fast Fourier transform (FFT). The objective lens (see Fig. 3.8) essentially performs a Fourier transform (FT) that results in a DP in the BFP and then an inverse FT that results in an image in the image plane. The FFT is an algorithm that once applied to a HRTEM image, outputs the DP. It's a kind of computational tool to get the DP from a digital HRTEM image and in a sense, is a translation from real space to reciprocal space.

Until now, our discussion has been around conventional TEM with the use of a parallel beam. STEM, which was briefly mentioned in the beginning of this chapter, utilizes a highly focused beam of electrons. The beam is scanned across the sample surface in a raster fashion, by use of scanning coils that deflect the beam, as in the SEM. At each spot the generated signal is simultaneously recorded by selected detectors, building up an image. Such a convergent beam is used to gain a highly localized signal and as the resolution of a STEM is limited by the diameter of the electron beam, it can lead to substantial improvements of the imaging properties and gives access to the sub-Ångström regime. In Fig. 3.9, a schematic drawing is shown of the various detectors used in STEM for the different imaging mode that will be discussed now. There are various imaging modes in STEM as well and the basic and most relevant to this thesis are:

- **Bright-field STEM (BFSTEM).** As in BFTEM, in this imaging mode the direct beam is selected, but in contrast to BFTEM, the direct beam is not selected by an aperture but by a specialized BF detector.

- **Dark-field STEM (DFSTEM).** Also, here as in DFTEM, the scattered beam on an angle is detected, but this is not achieved by an aperture, but by an annular (i.e. ring-shaped) dark field (ADF) detector. Basically, the detector is a ring, where the hole in the center is where the direct beam would go to the BF detector.

- **High-angle ADF STEM (HAADF-STEM).** Here, electrons scattered at more extreme angles (i.e. high-angle) are measured. A HAADF detector is utilized and basically it is an ADF detector with a larger diameter, thus omitting the direct beam and the smaller angle scattered electrons and so detecting only the large angle (> 50 mrad) scattered ones. The type of contrast that forms the image is known as Z-contrast (where Z is the atomic number). The strong Coulomb interaction of the negatively charged electrons with the positive potential of an atom core, leads to high-angle scattering (Rutherford scattering). The heavier (larger Z) the element is, the more extreme the scattering and consequently the contrast is approximately proportional to $Z^2$. So, by the HAADF-STEM method, heavier elements will appear brighter and lighter elements will appear darker, making this method ideal to distinguish heterostructures.
Energy dispersive X-ray (EDX) STEM. Until now, we've seen the various imaging modes that can be utilized by analyzing the electrons scattered by the sample. By taking advantage of X-rays generated by the electron beam and sample interaction, we have the ability to perform X-ray spectrometry in the TEM, which is one way to transform the TEM into an even more powerful analytical instrument. In this way, the chemical composition may be obtained in a quantitative way. The electrons can excite a core electron (from either the K, L or M shells) of the atoms of the sample, so that the core electron is ejected from the atom leaving a hole in its place. This hole is filled by an electron from a higher order shell. The transition is accompanied by energy emission in the form of X-rays. These X-rays are characteristic of the element they were emitted from, because the energy differences of the electron transitions from the outer to the inner shells are characteristic for each element. The emitted X-rays are collected by a spectrometer and may then be displayed as a spectrum or, better still, as a compositional image or “map”. Applying EDX in a STEM instrument, this information can be obtained with a spatial resolution approaching a nanometer or below and offers detection limits close to a single atom. This offers us elemental analysis on the nanoscale and is a powerful tool for analyzing heterostructures.

Figure 3.9. Schematic drawing of the STEM imaging mode. The BF mode implements a BF detector directly in the central transmitted beam path, the ADF detector (the cross-section is depicted) detects the scattered electrons while in the HAADF mode an even larger annular detector is implemented that picks up the signal from larger angles. Adapted from Ref.64.
All of the aforementioned imaging modes and techniques both for TEM and STEM assist in making the TEM a very powerful and analytical tool at the hand of the microscopist.

Sample preparation is an important aspect of TEM, albeit tedious from time to time, because of the universal TEM demand of thin samples for better imaging. The golden rule is “the thinner, the better” and depending on the original sample (e.g. bulk, thin film, NWs) there can be several paths to achieving this, some of which may be altogether improvised, adding a parameter of skill and ingenuity to it. As concerns this thesis, we will focus on preparation of samples from NWs. There are two views that we would like to acquire; the lateral one (i.e. side-view) and the longitudinal one (i.e. down the growth axis).

- For lateral views, a TEM grid is utilized. In our case, it consists of a mesh made out of copper (Cu) and between the holes of the mesh, an amorphous and holey carbon (C) film. A typical TEM grid can be seen in Fig. 3.10a. The C film has holes in it so that NWs deposited may have sections overlapping with the holes, so that the signal is as undisturbed as possible (i.e. the beam going only though the NW). The TEM grid has the advantage as well that it can be handled by its sides, meaning that the is as little handling of the NWs as possible. The deposition is as easy as taking the substrate sample with the NWs using tweezers and essentially “wiping” TEM grid across the sample. If it is performed in one single motion it has the benefit of depositing the NWs almost parallel to each other so the angular distribution of the NWs on the grid is as small as possible. This has the added benefit that when starting the TEM study, the tilting of the sample to find the correct zone axes is kept to a minimum.

- For longitudinal views, a thinning process is required due to the length of the NWs. This can be achieved (as in our case) by ion milling with the use of a focused ion beam (FIB). Summarily, it consists of a transfer of the NWs from the original substrate upon which they had been grown to a silicon oxide substrate in a controlled fashion by the use of a nano-manipulator. A protective platinum (Pt) coating in the form of a bar may be deposited normal to the NW growth axis. This is the part that will be protected from the ion beam and is exactly where the “slice” will be made which we want to use later in the TEM. The FIB milling with gallium (Ga) atoms on the one and the other side of the bar, will finally result in a thin cross-section of the NW. This thin slice is subsequently lifted-out from the substrate and mounted on a dedicated TEM sample support grid, after which the final thinning of the slice is performed.
Figure 3.10. (a), (b), (c) and (d) Optical microscopy images of a Cu TEM grid at consecutive magnifications. In (c) and (d) NWs deposited on the grid start to be distinguished. The NWs are GaP/Si core/shell; (e) BFTEM at low magnification. Encircled NW is the NW contained within a blue rectangular box in (c) and (d); (f) BFTEM image of the NW encircled in (e); (j) HAADF STEM of a section of the NW from (f).

As much as TEMs have helped us to gain insight and image the nanoscale, there are some issues that plague magnetic lenses and which can limit the microscope performance in substantial ways. These are:

- Spherical aberration ($C_s$), where the electrons that are further away from the axis of the lens are bent more strongly towards the axis, thus limiting our ability to magnify detail.
• Chromatic aberration ($C_c$), which refers to the color, \textit{i.e.} frequency of the electrons. Ideally the beam is monochromatic and indeed the beam that comes directly out of the gun is rather monochromatic, so the problem arises during the beam-specimen interaction. The emerging electrons have a range of frequencies and then the objective lens bends the lower energy electrons more. Logically, a thick specimen enhances this, so the "golden rule" of the TEM is to have as thin samples as possible. One can finally use energy filtering to make the emerging beam more monochromatic.

• Astigmatism, which occurs due to non-uniform magnetic fields in the TEM and which causes the electrons to spiral around the optic axis. This can be solved by stigmators that are small octupoles that introduce a compensating field to counter-balance the magnetic field inhomogeneities causing the astigmatism.

Many technologically advanced TEMs include corrections for these phenomena in order to further improve resolution, but significantly raise the price of the instrument. Corrections of $C_a$ and $C_c$ allow us to produce significantly sharper atomic-resolution images. Furthermore, by filtering out electrons of different wavelengths we can also image thicker specimens better.

The TEM measurements presented in this thesis were acquired by Dr. M. A. Verheijen and Dr. S. Conesa-Boj and were performed on two setups, namely the FEI Tecnai F30ST operated at 300 $kV$ acceleration voltage and the JEOL ARM 200F at 200 $kV$.

### 3.5 X-Ray Crystallography

X-ray crystallography is a tool which implements X-rays to identify the crystal structure of a crystalline solid as well as many other important structural parameters, \textit{e.g.} the lattice parameter. It is based on the principles of\textit{ diffraction} of X-rays by the ordered structure of a crystal and hence is known as X-ray diffraction (XRD).

When, through the wave-particle duality, we treat X-rays as electromagnetic radiation waves, they can be seen as scattering when they interact with the atoms of a crystal lattice. The waves scattered by the lattice atoms, cancel each other out in most directions by destructive interference. Under specific conditions that satisfy \textit{Bragg’s Law}, they can interfere constructively, leading to a signal that can be detected:

$$2d_{hkl} \sin \theta = n\lambda \quad \text{(Bragg’s Law)}$$

where $d_{hkl}$ is the spacing between the diffracting planes, $h, k$ and $l$ are the Miller indices, $\theta$ is the incident angle, $n$ is an integer and $\lambda$ is the X-ray...
wavelength (typical wavelengths used in XRD are hard X-rays around 1 Å). Fig. 3.11 shows a schematic representation of Bragg’s law. The Miller indices are used to define the orientation of the planes with respect to the unit cell. This equation tells us that when we scan the X-rays coming from the crystalline sample at different angles, we will detect signals at specific angles, which when coupled with the incoming radiation wavelength, can give us the lattice plane distance $d$.

![Figure 3.11](image)

Figure 3.11. (a) Schematic representation of the Bragg condition for constructive interference by parallel planes of atoms; (b) XRD experimental setup for the measurement of Bragg reflections. $K_i$ is the incident wave vector, $\omega$ is the angle between $K_i$ and the sample surface (note: this is different than $\theta$, which is the angle between incident wave vectors and lattice planes), $K_f$ is the scattered wave vector, $2\theta$ is the diffraction angle (defined as the angle between $K_i$ and $K_f$) and $Q$ is the momentum transfer ($Q = K_f - K_i$). All lie on the same plane that includes the normal to the sample surface. Adapted from Ref. 45

These signals produce a DP of regularly spaced spots known as reflections and are a depiction of reciprocal space. As mentioned in Ch. 3.4, each reflection (spot) in the DP (reciprocal space) corresponds to a set of planes in real space. In reciprocal space, or $k$-space, when the change in wave vector:

$$K = k_i - k_f$$

equals a reciprocal lattice vector:

$$K = G$$ (Laue condition)

a constructive interference happens. In the equations above, $K$ is the diffraction vector, $k_i$ is the incident wave vector, $k_f$ is the diffracted wave vector and $G$ is a reciprocal lattice vector$^{23}$. Based on this, we can construct the Ewald sphere in $k$-space, a very useful tool. The Ewald sphere (or Ewald construction as it is also known) is a geometric construct with a radius of the magnitude of the incident wave vector $k_i$ or the diffracted wave vector $k_f$ (see Fig. 3.12). This silently implies that the magnitude of both vectors is equal, meaning that we’re
considering elastic scattering. This leads to the important conclusion that the Laue condition is satisfied for reflections (spots) that lie on the surface of the Ewald sphere. So, by changing the angles, we can “access” the reflections that lie on the surface of the sphere and these reflections are the planes in real space.

![Figure 3.12. The Ewald sphere. Adapted from Ref.66](image)

There are different types of scans that we can perform to scan the angles (see Fig. 3.11 for the angles) and access different reflections:

- **ω scan.** In this scan, the sample is tilted so only ω changes and is also known as a “rocking scan”. This results in a movement perpendicular to $\mathbf{K}$ in k-space. The resulting plot is X-ray intensity against ω.

- **2θ scan.** In this scan, the source is fixed and only the detector moves so only 2θ changes and is also known as a “detector scan”. This results in a movement along the surface of the Ewald sphere. The resulting plot is X-ray intensity against 2θ.

- **ω − 2θ scan.** In this scan, the source is fixed and the sample rotates as well as the detector in such a way that

$$2\omega = 2\theta \Rightarrow \omega = \frac{1}{2} 2\theta$$

is satisfied and is also known as a “coupled scan”. This results in a movement along $\mathbf{K}$.

These scans allow us to move around in k-space and access different reflections.
Apart from constructing simple graphs in the form of “angle against intensity”, it is very useful to construct reciprocal space maps (RSMs). In this instance, we can scan \(2\theta\) for increments of \(\omega\) and essentially explore and map reciprocal space. Furthermore, instead of just normally plotting the \(\chi\) and \(y\) axes as \(2\theta\) and \(\omega\), we can plot \(Q_x\) and \(Q_y\), where:

\[
Q = \sqrt{Q_x^2 + Q_y^2}
\]

and

\[
Q \equiv K
\]

Based on the RSM, we are able to calculate d-spacing, lattice mismatch, layer thickness, layer relaxation and strain.

An important consideration to take into account is whether the crystal planes are symmetrical or asymmetrical. Simply put, symmetrical planes are the planes that are parallel to the surface of the sample, while asymmetrical planes are the planes that are at an angle relative to the surface of the sample (see Fig. 3.13). This needs to be taken into account, in order to align the sample accordingly.

![Figure 3.13](image)

Figure 3.13. (a) A symmetric scan; (b) an asymmetric scan. Adapted from Ref.66

Let’s imagine for a moment a heterostructure with the assumption that each of the materials is totally relaxed (see Fig. 3.14a). In this case, the DP will be a superposition of two DPs, namely each one that corresponds to the two materials. This is because of relaxation, each has adopted its native lattice parameter and hence, d-spacing. Each DP will be shifted with respect to the other. Performing a symmetrical scan of the symmetrical planes or an asymmetrical scan of the asymmetric planes, will give us access to some reflections of k-space. These will provide information on the d-spacing of the two materials. In Fig. 3.14c, a depiction is presented of the reflections that are observed when performing a symmetric and an asymmetric scan of the structure depicted in Fig. 3.14a. Now if we suppose that one of the materials has adapted its unit cells to match the other one’s (i.e. pseudomorphic growth), it will be
strained (see Fig. 3.14b). While doing this, one of the unit cell dimensions will match the other material’s cell (becoming stretched or compressed); while in the perpendicular direction it will be the opposite. This straining will only show up in an asymmetrical scan. That is logical; the in-plane lattice parameter of the materials is the same for both, but for the strained one that has a skewed unit cell in the perpendicular direction, the asymmetric planes will be shifted. Thus, this will only show up in an asymmetric scan. In Fig. 3.14d, a depiction is presented of the reflections that are observed when performing a symmetric and an asymmetric scan of the structure depicted in Fig. 3.14b. As can be seen, the symmetric scan presents the same reflections as the symmetric scan of Fig. 3.14c. So, in this case no distinction is made. But when the asymmetric scan is performed, then the (blue) spot corresponding to material (ii) is shifted compared to the asymmetric scan of Fig. 3.14c. So, in this case a distinction is made and we can extrapolate that material (ii) has grown in a pseudomorphic way onto material (i).

Figure 3.14. (a) Material (ii), which has been grown on (i), has adopted its native unit cell dimensions and thus is fully relaxed; (b) material (ii) has adapted one dimension of its unit cell to material (i), while the perpendicular dimension has been stretched accordingly. Thus, material (ii) is strained (pseudomorphic growth); (c) a symmetric and an asymmetric scan of case (a). The reflections are shifted with respect to each other due to each material having its own unit cell dimensions (hence d-spacing); (d) a symmetric and an asymmetric scan of case (b). Here the reflections of material (i) are the same as in (c), but now the reflection of material (ii) in the asymmetric scan is shifted, due to the deformation of the unit cell. Courtesy of Prof. Dr. J. Stangl and adapted from Ref. 66
The XRD measurements presented in this thesis were carried out at the European Synchrotron Radiation Facility (ESRF). XRD from synchrotron radiation has the benefit of a high photon flux beam, a broad spectrum of wavelengths, high brilliance and polarization. Compared to standard XRD lab equipment, a synchrotron source is $\sim 10^9$ times more brilliant. Now compared to TEM, XRD offers the advantage of measuring ensembles of NWs, has a much better resolution in terms of lattice spacings, is not destructive (in the sense that the NWs can be measured as grown on the substrate, but in TEM they need to be wiped off to a grid) and sample preparation can take significant amount of time for TEM. On the other hand, TEM provides a more detailed analysis on the atomic scale, allowing for the visualization of the crystal structure, defects, minority phases, outer sample morphology and compositional and strain variations.

The XRD measurements were performed by Dr. T. Etzelstorfer, Univ. Prof. J. Stangl and Dr. D. Kriegner.

### 3.6 Raman Spectroscopy

Raman spectroscopy is a technique that is used to measure vibrational and rotational and other low-frequency modes in a system. In solid-state physics it can be used, amongst other things, to characterize materials, because solid materials have characteristic phonon modes that contribute to their identification. The technique is based on Raman scattering, which is inelastic, of monochromatic light in the near infrared (IR) ($0.75 - 1.4 \mu m$), visible ($380 - 700 nm$) and near ultraviolet (UV) ($300 - 400 nm$) ranges. A laser beam, operating in the above reported regions, passes through the sample and interacts with the polarizable electron density and bonds of the sample’s molecules. A photon can excite a molecule to an exited rovibronic state (i.e. rotational/vibrational state), which results in its transition to a virtual energy state. Afterwards, the molecule transitions back to a lower energy state and a photon is emitted. Herein we can find the inelastic nature of this scattering. If the final energy state is different than the one before excitation, the energy of the emitted photon will be of either lower energy ($Stokes$ Raman scattering) or higher energy ($anti-Stokes$ Raman scattering) than that of the impinging photon (Fig. 3.15). This contrasts to Raleigh scattering, where the energy of the final state is the same as the one before excitation, resulting in an emitted photon of the same energy as the one impinging, making this type of scattering elastic.

The resulting spectrum obtained is the Raman spectrum and is a plot of the intensity of the scattered light as a function of its frequency difference $\Delta \omega$ from the impinging light and is given in inverse units of length:

$$\Delta \omega = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$$
where $\Delta \omega$ is the frequency shift (known as Raman shift), $\lambda_0^{-1}$ is the frequency of the impinging photons, $\lambda_0$ is the wavelength of the impinging photons, $\lambda_1^{-1}$ is the frequency of the scattered photons and $\lambda_1$ is the wavelength of the scattered photons. In this sense, the most frequently used unit to express $\Delta \omega$ is $cm^{-1}$. Further insights can be obtained by polarized Raman analysis. This is achieved by using plane polarized laser excitation and a polarization analyzer. With this methodology, the *depolarization ratio* can be measured, which is the intensity ratio of the perpendicular component to the parallel component of the Raman scattered light. This technique is useful to study and differentiate between polymorphs of the same material, *i.e.* different crystallizations (crystal structures) of the same material. Polarized light only gives access to some of the Raman active modes, so we can identify the crystal structure by rotating the polarization and gain access to the other modes. This happens due to the crystal symmetry.

![Diagram of Raman and Rayleigh scattering](image)

**Figure 3.15.** Raman (inelastic) and Rayleigh (elastic) scattering. In Rayleigh scattering the incident and scattered photons have the same energy, whilst in Raman scattering the energy is different: in Stokes Raman scattering the scattered photon has less energy than the incident photon (atom or molecule absorbs energy), while in anti-Stokes Raman scattering the scattered photon has more energy than the incident photon (atom or molecule loses energy). This is due to the fact that for Stokes Raman scattering the final “de-excited” state is still higher than the original ground state, while for anti-Stokes Raman scattering the final “de-excited” state is lower than the one before excitation, because the atom or molecule was in an already excited state. Adapted from Ref.67.
Chapter 4 - Defects in Hexagonal Silicon

Semiconductor nanowires have increased the palette of possible heterostructures thanks to their more effective strain relaxation. Among these, core/shell heterostructures are much more sensitive to strain than axial ones. The formation of misfit dislocations depends both on the lattice mismatch and relative dimensions of the core and the shell. Here we show for the first time the existence of a new kind of defect in core/shell nanowires: cracks. These defects do not originate from a lattice mismatch (we demonstrate their appearance in an essentially zero-mismatch system) but from the thermal history during the growth of the nanowires. Crack defects further lead to the development of secondary defects, such as type-I$_1$ stacking faults and Frank-type dislocations. These results provide crucial information with important implications for the optimized synthesis of nanowire-based core/shell heterostructures.

4.1 Introduction

The unique filamentary nature of nanowires has opened the path towards obtaining new combinations of semiconductors in three dimensions in a nearly defect-free manner, thereby allowing functionalities not possible in the thin film form$^{68-73}$. Mismatched materials can be integrated in the same nanowire forming heterojunctions, quantum dots and barriers. Interestingly, it is even possible to combine semiconductors of different families such as III-Vs and group IV materials$^{74,75}$. In this respect, the integration of Si with materials of the III-V groups is particularly relevant for expanding the wealth of optical and electronic applications with nanowires$^{34,52,76}$.

Core/shell heterostructures, in particular, offer many advantages like the possibility to efficiently release strain radially. Another benefit of core/shell systems is that the shell, which is subsequently grown around the core, might adopt, under specific conditions, the same crystalline structure as the latter. Crystalline phases otherwise not stable in bulk form can be obtained in this way, in a consistent and reproducible manner. This was demonstrated for the first time in the GaP/Si system$^{74}$. Thanks to this crystalline structure transfer property, the Si shell could adopt the hexagonal crystalline phase of the GaP core, even though bulk Si, under standard conditions, is always found in the diamond cubic structure.

Defect formation in core/shell systems has been extensively studied in literature$^{77-79}$. One of the main sources of defect formation is the lattice mismatch between the shell and the core. In this case, mechanical stress leads to plastic deformation in the shell, which in turn translates into the formation of misfit dislocations at the core/shell interface$^{80}$. Furthermore, strain relaxation
can also lead to the formation of surface roughness\textsuperscript{81}, the formation of islands, and also of quantum dots\textsuperscript{82}.

One condition for core-shell systems to be used as building blocks in realistic nanodevices is the achievement of an extremely low density of structural defects\textsuperscript{83}. For instance, for optoelectronic applications, crystalline defects degrade electric transport properties by playing the role of recombination centres\textsuperscript{84}. For this reason, it is of utmost importance to first fully characterize and then understand defect formation in core/shell systems for a variety of material combinations, which in turn will allow the optimization of the growth conditions towards the achievement of defect-free nanowire structures\textsuperscript{85}.

Until recently, the quantification of defect formation in core/shell nanowires has been limited to lattice-mismatched systems. To the best of our knowledge, there are no reports of defect characterization in systems composed by materials with similar lattice parameters. In this work, we demonstrate for the first time that, also for these systems, defect formation can be ubiquitous. As we will show, the mechanisms of defect formation are tightly related to specific details of the growth process. We illustrate our findings in the specific case of GaP/Si core/shell nanowires. We report on the formation of a type of defects, known as cracks, never before observed in nanowires. The origin of these cracks is driven by the thermal history of the growth process, which can induce a Brittle-to-Ductile Transition (BDT) in the Si shell. Remarkably, these cracks further develop into another type of secondary defects characteristic of the hexagonal crystal structure: intrinsic staking faults of type-\textit{I\textsubscript{1}}. We explain how these secondary defects are correlated, for instance, how nearby stacking faults induce Frank-type dislocations parallel to the growth axis.

Up to now, both experimental studies and theoretical models of defect formation in core-shell nanowires have been restricted to mismatched materials, where the appearance of defects is driven mainly by differences in the geometry and crystalline structure of the core and shell materials. Our results show, for the first time, that the formation of defects can also be ubiquitous in materials with similar lattice parameters, becoming a limiting factor for their optoelectronic applications. The understanding of the mechanisms that underlie this unexpected formation of crack defects provides crucial information to devise novel growth conditions and achieve defect-free GaP/Si core/shell nanowires, and should be important to refine existing theoretical models of defect formation.

\section*{4.2 Growth}

Core/shell GaP/Si nanowires were grown in a low-pressure (50 mbar) Aixtron CCS MOVPE reactor. Two different samples have been studied, where the
Si shell was deposited at two different temperatures, 750 °C and 800 °C. In Fig. 4.1a GaP substrate NWs can be seen, while in Figs. 4.1b and 4.1c, GaP/Si core/shell NWs are presented, grown at 750 °C and 800 °C, respectively.

**Figure 4.1.** (a), (b) and (c) Scanning Electron Microscopy (SEM) images corresponding to the GaP nanowires, and GaP/Si core-shell nanowires, where the Si shell was deposited at 750 °C and 800 °C, respectively. The GaP/Si core-shell nanowires grown at 750 °C have a Vapor-Liquid-Solid growth on the top, while the nanowires grown at 800 °C do not exhibit such a pronounced Si VLS growth on the top.

The GaP core was grown using the Vapor-Liquid-Solid mechanism with Au as catalyst. These Au catalyst seeds, with a diameter of 125 nm each, formed a square pattern with a 500 nm pitch, and were deposited on GaP (111)_B substrates with the nanoimprint technique. The GaP core was grown at a temperature of 750 °C^{60}, employing a flow of PH₃ and TMG as precursor gases. H₂ was used as a carrier gas for the precursors and the total flow into the reactor was 8.2 l/min. Once the growth of the core was completed, a cool-down step followed until a temperature of 200 °C was reached^{74}. During the cool-down step, the PH₃ flow was continued to protect the GaP nanowires from desorption. When the temperature reached 200 °C, the PH₃ flow was turned off and a flow of disilane precursor gas with a molar fraction of 1.04 × 10⁻⁴ was commenced for the following 20 min.

For the growth of the Si shell, the temperature was subsequently ramped up to 750 °C (800 °C) for a time period of 10 min, while the Si₂H₆ flow was kept on. Following this, the reactor was kept at a constant temperature of 750 °C (800 °C) for 60 min (52 min, respectively). This duration was determined by the requirement that a uniform shell thickness should be achieved for the samples at the two different temperatures. In the final step, the heating elements were switched off, the flow of Si₂H₆ was terminated and the reactor was allowed to cool down to room temperature.
4.3 Structural Characterization

In order to explore the nature of the GaP/Si core/shell nanowires, STEM with EDX spectroscopy for elemental analysis was used. Fig. 4.2a corresponds to a

![Figure 4.2](image)

**Figure 4.2.** (a) HAADF image of a representative GaP/Si core/shell nanowire; (b) compositional map corresponding to the green rectangle in (a), with Si shown in green and GaP in purple; (c) schematic illustration of the viewpoint used for the HRTEM analysis. The nanowire contains \{10\bar{1}0\} side facets; (d) and (e) HRTEM images of another representative GaP/Si core/shell nanowire exhibiting several planar defects lying on the (0001) planes, where the Si shell was deposited at 750 °C and 800 °C, respectively; (f) low magnification BFTEM image of a single GaP nanowire exhibiting few stacking faults (marked by black arrows) and (g) TEM image along the [11\bar{2}0] zone axis of the GaP/Si core/shell exhibiting the transferred stacking fault defect from the GaP core to the Si shell.
HAADF image acquired in STEM. Such type of image is highly sensitive to the atomic number (Z), so the bright area represents the GaP core and the dark area corresponds to the Si shell. EDX elemental mapping (Fig. 4.2b) further demonstrates that the nanowires display a GaP/Si core/shell structure.

Figs. 4.2d and 4.2e display typical TEM images of these crystalline GaP/Si core/shell nanowires viewed along the [11̅20] zone axis (Fig. 4.2c), where the Si shell was deposited at different temperatures of 750 °C (Fig. 4.2d) and 800 °C (Fig. 4.2e), respectively. Notice that the Si shell thickness turns out to be different, being around 20 min for the Si deposited at 750 °C and around 40 min for the one deposited at 800 °C, because the Si deposition time is different. Fast Fourier transform (FFT) analysis reveals that these nanowires are single crystalline exhibiting the hexagonal structure. Typical TEM images indicate that these core/shell nanowires include several defects lying in the radial direction, mainly localized on the facets and edges of the Si shell. The two samples have quite a different morphology. For the core/shell nanowires where the Si shell was deposited at 800 °C, a remarkable feature observed is the presence of “elbows”, that is, small irregularities on the Si shell surface, as seen in the inset of Fig. 4.2e.

A feature common to the two samples is the presence of stacking faults crossing the full diameter of the nanowire, that is, defects that arise both in the GaP core and the Si shell. This type of defect is generated during the VLS growth of the GaP core, see Fig. 4.2f, and then transferred to the Si shell during epitaxial shell growth, see Fig. 4.2g. Therefore, the density of this type of defects in the Si shell is directly related to the density of defects in the original GaP core.

In Fig. 4.3c we show a high-resolution TEM image of a region of the Si shell revealing the presence of two intrinsic stacking faults type-I$_1$ (marked by a yellow rectangle). In order to quantitatively identify the presence of this type of defects, we compute the phase shift between the two planar defects using Geometrical Phase Analysis. By selecting the $g = (1\bar{1}00)$ Bragg reflection and taking the intermediate region between the two yellow rectangles as a reference, we have extracted the corresponding phase profiles, averaging over the region marked with the black dashed rectangle in Fig. 4.3d. From this profile, a phase shift of approximately 2.1 rad is estimated both in the upper (labeled as I) and lower (labeled as II) regions as compared to the intermediate one, as can be seen in Fig. 4.3e. Therefore, the resulting displacement turns out to be $1/3[1\bar{1}00]$. This is precisely the characteristic value for the intrinsic stacking fault of type-I$_1$ in wurtzite, thus confirming that indeed they are present in our nanowires.
Figure 4.3. (a) Low magnification bright field TEM image of a single GaP nanowire exhibiting few transversal defects (marked by black arrows); (b) high-resolution TEM image along the [11\(\bar{2}0\)] zone axis of the GaP/Si core-shell exhibiting the defect transferred from the core to the shell; (c) HRTEM image of the region of the Si shell where the planar defects are indicated by a black arrows, and the inset is the corresponding fast Fourier transform; (b) phase image obtained by selecting the \(g = (1\overline{1}00)\) Bragg reflection (marked by a white circle in the inset in (c)); (e) Phase profile horizontally averaged in the black dashed rectangle in (d).

Fourier filtered analysis revealed that no misfit dislocations at the interface between GaP and Si were present (Fig. 4.3c) implying that strain relaxation due to the mismatch between the lattice constants at the interface plays only a minor role in defect formation. This is not the case in other core/shell systems, such as Ge/Si\(^{79,86}\), GaAs/Si\(^{87}\), InAs/GaAs,\(^{88}\) characterized by a substantially larger lattice mismatch, and where such misfit dislocations have been reported. The absence of misfit dislocations in GaP/Si nanowires is the first hint suggesting that the relaxation mechanism that leads to defect formation in our system does not depend on the characteristics of the crystalline structure and geometry of the core and shell materials, but instead, as we discuss below, on the specific details of the growth conditions, in particular the thermal history.

4.4 Fingerprinting Crack Defects

The structural properties of these defects are further examined by HRTEM and multi-slice simulation. First, we consider the GaP/Si core/shell nanowires
where the shell was deposited at 750 °C. Fig. 4.4a shows a HRTEM image of one of these defects localized at the edge of the Si shell. When an intensity profile is recorded along the axial direction (Fig. 4.4e), a depletion of the intensity is observed (indicated by red arrows) when crossing the defect, revealing the presence of what turns out to be a fracture on the Si shell surface. Interestingly, Fourier analysis indicates that this defect does not seem to arise from an alteration of the regular sequence in the stacking of lattice planes of the Si shell.

Figure 4.4. (a) HRTEM image along the \([1\bar{1}20]\) direction of a representative short defect (marked with a red solid rectangle); (b) and FFT of (a); (c) (d) filtered fast Fourier images obtained from the \((0001)\) and \((1\bar{1}00)\) Bragg reflections, respectively; (e) intensity profile performed crossing the defect in the axial direction, where the position of the crossing is marked with two arrows.

Fig. 4.4a corresponds to an HRTEM image of a crack in the Si shell and Fig. 4.4b is the corresponding FFT. By applying a mask on the \((0001)\) and \((1\bar{1}00)\) Bragg reflections, we determine the relative Bragg filtered lattice fringes, shown in Figs. 4.4c and 4.4d, respectively. It indicates that this defect does not seem to arise from an alteration of the regular sequence in the stacking of lattice planes of Si shell.

This type of defect is known in literature as a crack defect. Previous studies of cracks have been mainly focused in two-dimensional systems\(^89\), but never in nanowires. Likewise, a substantial number of studies based on large-scale molecular simulations in order to characterize the formation and extension of crack defects have been performed, but restricted to thin films\(^90-92\). We provide
here evidence for the first time that crack defects can develop in one-dimensional systems, in particular in core/shell nanowires.

In the following section, we perform a multi-slice simulation using the Java Electron Microscopy Image Simulation (JEMS) software supplemented with an atomic model of the crack (see Fig. 4.5c) constructed using the Rhodius program in order to evaluate more precisely the atomic arrangement of the crack defect.

Figure 4.5. (a) HRTEM image along the [11\overline{2}0] direction of a representative short defect (marked with a red solid rectangle); (b) intensity profile performed crossing the defect in the axial direction, where the position of the crack is marked with two red arrows; (c) Rhodius atomic model of a crack lying on the edge of a hexagonal Si matrix. On the left, the atomic model is viewed in the [11\overline{2}0] zone axis and on the right side the atomic model is a bit tilted off this axis, in order to better visualize the crack; (d) results of the JEMS multi-slice simulation of the crack modeled in (c) viewed in the [11\overline{2}0] zone axis, were the various simulations were obtained using defocus values from 65.1 \text{ nm} to 67.7 \text{ nm}.
The crack defect is modeled as a local fracture, that is, a region where the separation between two adjacent atomic layers is increased. The crack is then embedded into a hexagonal Si matrix viewed in the $[\overline{1}120]$ zone axis. The parameters used to reproduce the settings of the Tecnai Osiris microscope used in this work were the following: acceleration voltage of $200\, kV$, $C_s = 1.2\, mm$, $C_C = 2\, mm$ and energy spread of $0.7\, eV$. Fig. 4.5d presents the resulting series of simulated images for different defocus values. By comparing the HRTEM image (Fig. 4.5a) and the simulated images (Fig. 4.5d), a good agreement is obtained for $67.2\, nm$ focal distance. The agreement of the HRTEM measurements with the atomic simulations provides further confirmation of the nature of the crack defect.

Remarkably, another important observation emerging from TEM analysis is the presence of half-dislocation loops. It has been demonstrated that the nucleation of this type of defect is highly sensitive to the growth temperature and they can originate from pre-existing crystal defects, such as dislocations or cracks$^{95}$. 

### 4.5 From Cracks to Stacking Faults

Next, we carefully examine the sample where the Si shell was grown at $800\, ^\circ C$. Interestingly, there is a substantial difference in the density and type of defects observed between the two samples. While crack defects are still present, their density has decreased, and we find instead that in some cases they have been replaced by type-$I_1$ stacking faults, a defect characteristic of the hexagonal crystalline phase (Figs. 4.6a and 4.6b). In addition, further TEM observations reveal also the presence of Frank-type dislocations, vertical defects that appear linking two different type-$I_1$ stacking faults. In turn, these new dislocations are found to act as the seed of further secondary type-$I_1$ stacking faults (Fig. 4.6c).

A suggested mechanism to generate stacking faults of type-$I_1$, as well as Frank-type dislocations, from the presence of cracks has been suggested in Ref.$^{96}$. This mechanism is illustrated in Figs. 4.6e-g, where we represent schematically the different steps of the formation process of a type-$I_1$ stacking fault and of Frank-type dislocations from a pre-existing crack defect. The first step is the presence of a crack defect, which induces the collapse of the neighboring atomic layers, see Fig. 4.6f. This collapse leads in turn to a rearrangement of the atomic layers that effectively results in a type-$I_1$ stacking fault, Fig. 4.6g. This way, the next layer that will be grown (marked with orange atoms) will be affected by this stacking fault and generate a vertical Frank-type defect, see Fig. 4.6g. In particular, the small cubic crystalline region in Fig. 4.6d can be understood as the extension of a stacking fault of type-$I_1$: indeed, this stacking fault in the hexagonal structure is equivalent to a monolayer of the cubic structure. Our
model thus explains the formation of this initial monolayer characteristic of the cubic structure; afterwards, all subsequent Si layers deposited will also adopt the cubic crystalline structure, explaining the formation of this relatively large cubic region, or “elbow” (Fig. 4.6d), in the Si shell.

![Figure 4.6](image)

**Figure 4.6.** (a) HRTEM image showing the interaction between cracks; (b), (c) and (d) magnification of the region marked with a dashed, dot-dashed and solid white rectangle in (a), respectively; (e) and (f) schematic illustration of the generation of a type-1 stacking fault (SF) from a crack defect; (g) a Frank Partial dislocation (green vertical line) resulting from the rearrangement of the atoms.

Our results provide strong evidence that, perhaps unexpectedly and despite the small lattice mismatch between the GaP core and the Si shell, a rich pattern of structural defects appears in the Si shell. Therefore, our findings clearly illustrate that the relaxation mechanism leading to defect formation in essentially zero-mismatch materials can be driven by the specific growth conditions, rather than by the geometry and crystalline structure of the core and shell materials. As we discuss now, the thermal history during growth is the crucial ingredient.
4.6 Brittle-to-Ductile Transition

In other systems like thin films, the generation of crack defects is known to be linked to a thermal shock experienced at a certain point during the growth process\cite{97,98}. This mechanism appears to be also at work for nanowires: during their growth, the formation of a thermal gradient in the system leads to a thermal shock, which in turn induces an expansion of the material by an amount that differs region by region. Therefore, crack formation in core/shell nanowires can be understood to arise from the thermally induced strain gradient in the system, suggesting that this excess of strain is at the origin of crack formation. This point is further examined in the supplementary information section IV, where a detailed strain analysis around the crack defect region is reported.

The formation of cracks, as well as their development into other types of defects, has been reported to be dependent on the BDT behavior. Many semiconductor materials exhibit such a transition when their temperature is raised\cite{97,98}. These phenomena have been observed for instance in Si wafers exposed to thermal stress\cite{99}. Ref.\cite{100} shows that crack defect generation takes place in a narrow range of temperatures around 620 °C, and that exceeding this value the crack tends either to propagate along the crystalline structure or to seed the formation of a secondary crack. Ref.\cite{95} provides the evidence that the BDT in Si is related to the formation and growth of a plastic zone around the crack tip. Theoretical calculations also support this explanation\cite{92}. For instance, in Ref.\cite{101} the authors develop an atomic model to illustrate this transition from the crack formation to the dislocation emission from the crack tip under certain variations of temperature. Interestingly, it has also been demonstrated that the temperature at which the BDT takes place is reduced as the sample size decreases. As an illustration, Ref.\cite{102} demonstrates that the BDT temperature for single crystal Si can be reduced from the bulk, where the BDT temperature is about 545 °C, by more than 30% in one-dimensional nanostructures, such as nanowires.

In our case the deposition of the Si shell was performed in two different steps in terms of temperature, first at 200 °C and then at either 750 °C or 800 °C. The main difference between the two samples is that, for the case with a higher Si deposition temperature, in addition to cracks, the generation of a rich variety of secondary defects is observed. This suggests that at 800 °C the shell material has become ductile, since under these conditions cracks can seed additional defects. Our studies point to the direction of the hexagonal Si BDT temperature lying in the range between 750 °C and 800 °C. In this context, the presence of secondary defects is naturally understood in terms of the previous existence of cracks. Our observations that the sample where the Si shell was deposited at 750 °C only exhibits crack defects suggest that the secondary defects are generated by the differences in the temperature of the second step of the growth, from 750 °C and
800 °C. This difference is enough to induce local changes of the dilatation coefficient in the crystalline structure of the Si shell and thereby allowing the formation of type-$I_1$ stacking faults and Frank-type dislocations.

It is known that at low temperatures Si tends to be more brittle than ductile, while the latter behavior is restricted to growth processes carried out at high temperatures\textsuperscript{102}. If this is the underlying mechanism that drives defect formation in our system, a potentially effective method to decrease their density would be to skip altogether this soft transition, for instance by avoiding strong variations in the temperature of the system during growth. This strategy would avoid sudden local changes of the dilatation coefficient in the crystalline structure in the brittle regime, which is the underlying mechanism that leads to the nucleation of cracks.

In summary, in this work we have provided an accurate characterization and quantitative understanding of defect formation in GaP/Si core/shell systems. We have shown that the formation of defects is driven by strain relaxation, arising not from the small difference in the lattice parameters of the core and shell materials, but rather from the specific details of the growth process, in particular from the thermal history. Our results have led us to propose an alternative growth strategy to achieve defect-free hybrid core/shell structures.
Chapter 5 - Hexagonal Silicon

Si, arguably the most important technological semiconductor, is predicted to exhibit a range of new and interesting properties when grown in the hexagonal crystal structure. To obtain pure hexagonal Si is a great challenge since it naturally crystallizes in the diamond cubic structure. Here, we demonstrate the fabrication of pure and stable hexagonal silicon evidenced by structural characterization. In our approach, we transfer the hexagonal crystal structure from a template hexagonal gallium phosphide nanowire to an epitaxially grown silicon shell, such that hexagonal silicon is formed. The typical ABABAB... stacking of the hexagonal structure is shown by aberration-corrected imaging in transmission electron microscopy. In addition, X-ray diffraction measurements show the high crystalline purity of the material. We further show that this material is stable up to 9 GPa pressure. With this development, we open the way for exploring its optical, electrical, superconducting, and mechanical properties.

5.1 Introduction

The hexagonal crystal structure of Si, otherwise known as lonsdaleite (space group $D_{6h}^4$ in Schönflies notation), and its promise of novel properties in comparison to bulk diamond cubic structure Si have recently sparked interest in studying these properties because stable regions of pure hexagonal phase Si have not been unambiguously identified up to date. So far, it has not been possible to study these properties because large and stable regions of pure hexagonal phase Si have not been unambiguously identified up to date. There have been claims about the growth of hexagonal Si with various methods on the nano-scale; Si NWs grown by the VLS method, high pressure studies with the diamond anvil cell technique on cubic Si substrates and microcrystallites deposited during laser ablation of SiO$_2$ films. In all cases, it is difficult to control the formation of the crystal phase, but more importantly, explicit structural characterization is lacking. Recent studies have demonstrated that great care should be exercised when interpreting diffraction patterns claiming hexagonal Si. It cannot be ruled out, that in the studies that claim hexagonal Si, the diffraction patterns ascribed as belonging to the hexagonal phase in fact originate from defected diamond cubic Si. In this report, we develop a new method to fabricate single-crystalline hexagonal Si and we unambiguously demonstrate the characteristics of the pure hexagonal crystal lattice of Si.

5.2 Growth

We employ the crystal structure transfer method in which we epitaxially grow Si shells on a template of pure hexagonal crystal structure GaP NWs.
grown by the VLS mechanism utilizing Au catalyst seeds. The Au catalyst particles were deposited with the nanoimprint technique on GaP (111)\textsubscript{B} substrates. As the GaP core growth was performed under hydrogen chloride gas (HCl) flow to suppress the radial overgrowth of the wires, a GaP shell was grown afterwards in order to remove any surface chlorine (Cl) passivation. For this purpose, once the growth of the core was completed, a cool-down step followed until a temperature of 690 °C. In this step, the PH\textsubscript{3} flow was continued to protect the GaP NWs from desorbing. When the temperature of 690 °C was reached, the PH\textsubscript{3} flow was modified to a molar fraction of 1.10 × 10\textsuperscript{-2} and the TMGa to a molar fraction of 6.75 × 10\textsuperscript{-5}, resulting in a high V/III ratio of 162. This was done in order to favor Vapor-Solid (VS) growth over VLS growth and resulted in a 15 nm thick GaP shell.

Following this, the TMGa flow was terminated and the growth chamber was ramped-up to a temperature of 900 °C in a PH\textsubscript{3} environment. Once the considerably high temperature of 900 °C was reached, the PH\textsubscript{3} flow was turned off and disilane with a high molar fraction of 1.04 × 10\textsuperscript{-4} was introduced in order to commence the growth of the hexagonal Si shell. By ramping-up the temperature in a PH\textsubscript{3} environment and introducing disilane only at 900 °C, we are able to obtain single-crystalline hexagonal Si of high quality\textsuperscript{21}. In the final step, the heating elements were switched off, the flow of Si\textsubscript{2}H\textsubscript{6} was terminated and the reactor was allowed to cool down to room temperature.

In Ref. \textsuperscript{74}, after GaP core growth, the growth interruption method was employed in order to prevent Si VLS growth from the AuGa eutectic, followed by a final growth temperature of 550 °C. In this work however, we heat up to 900 °C after GaP core growth using PH\textsubscript{3} in order to protect the GaP core from desorption and subsequently start the growth of the Si shell. The growth at this high temperature was done in order to obtain thick single-crystalline hexagonal Si of high quality, avoiding any defect formation\textsuperscript{21}. By following these steps, we are able to achieve a high density of GaP/Si core/shell NWs, as can be observed in the cross-sectional SEM image in Fig. 5.1a, which shows an array of GaP/Si core/shell NWs with a length of 7 μm and diameters of 250 nm. The robustness of our strategy, which leads to single-crystalline hexagonal Si shells, has been verified by growing shells with a thickness between 5 – 170 nm.

The composition of the wires was studied by EDX spectroscopy in TEM, shown in Fig. 5.1d. The elemental map confirms the GaP/Si core/shell structure. The corresponding compositional line profile in Fig. 5.1e shows that we have a pure Si shell with a thickness of 75 nm. A low magnification BFTEM image of a representative [0001] (Miller-Bravais notation) oriented GaP/Si core/shell NW, shown in Fig. 5.1b, exhibits a low defect density along the entire length of the NW. The corresponding HRTEM image (Fig. 5.1c), oriented in the [1\textbar{1}20] zone axis, confirms that the core/shell structure is a single crystal, and illustrates the perfect epitaxy of the Si shell on the GaP core. The associated FFT (Fig. 5.1c,
inset) provides further evidence that the core/shell is a single-crystalline phase, and indicates that it is a HCP structure with (0001) growth direction.

The only type of defects observed are stacking faults (SFs) transferred from the GaP core to the Si shell, with a density of around 1 SF/µm throughout the whole wire, except close to the top, where SFs are formed during cooling down after GaP growth. This can be seen in more detail in Fig. 5.2 and even in the SEM imaging (Fig. 5.1a). In Fig. 5.2a we show a TEM image taken after GaP core growth. During this part of the process the TMGa flow has been terminated, but the PH₃ flow has been kept on in order to protect the NW from desorption at the high temperature of 750 °C. At this time, the Au/Ga eutectic droplet is still

**Figure 5.1.** Morphology overview of GaP/Si core/shell NWs. (a) Cross-sectional SEM image of a representative sample of GaP/Si core/shell NWs. Scale bar corresponds to 1 µm. (b) Low magnification BF-TEM image of one of the NWs from the sample shown in (a) exhibiting an untapered shape. Scale bar in (b) is 200 nm (1 µm in the inset). (c) High-resolution TEM image of the GaP/Si interface with the corresponding FFT in the inset. Scale bar is 20 nm. (d) and (e) EDX compositional map (scale bar is 100 nm) and the corresponding line scan taken across the NW diameter as indicated by the white arrow in (d). The line scan has been obtained integrating the EDX map in the region marked by a white dashed box.
supersaturated with Ga, meaning that Ga will still precipitate out of it. This, in combination with the PH$_3$ flow means that there are still conditions satisfied to continue nucleating layers under the droplet, essentially meaning that growth will continue for a little longer, until the droplet has reached a stable minimum solubility of Ga and no more Ga will be precipitating out of it. The defects are generated due to the fact that the system was not any more at the correct growth temperature -since it was in the cooling-down step- and the HCl flow was not employed any more. Furthermore, this defect structure will be transferred to the Si shell as can be seen in Fig. 5.2b. The Si shell growth rate in this defected top part is a little faster than the growth rate of the hexagonal Si shell in the rest of the wire, which accounts for the characteristic bulge that is observed at the top.

![Figure 5.2](image)

**Figure 5.2.** Defected top part. (a) bright field TEM of a representative GaP NW core top part. Scale bar 50 nm. (b) bright field TEM of a representative GaP/Si core/shell NW top part. Scale bar is 200 nm.

In order to prove the hexagonal crystal structure of the Si, we image a thin Si shell at high-resolution HAADF (HR-HAADF) STEM mode, see Fig. 5.3a. The epitaxial quality of the GaP/Si interface taken along the [11\(\bar{2}\)0] zone axis is demonstrated, showcasing the defect-free growth of the hexagonal Si shell around the GaP core. A magnified image of the atomic rows exhibiting the GaP/Si interface is shown in Fig. 5.3b, where the \textit{ABABAB...} stacking sequence of atomic bilayers characteristic of hexagonal crystal systems in the (0001) direction is clearly visible.

This characteristic stacking sequence was reproduced by the atomic model of hexagonal Si grown in the (0001) direction and imaged in the [11\(\bar{2}\)0] view, see Fig. 5.3c, further strengthening our interpretation. Fig. 5.3d shows the spatial resolution of Si dumbbells, from which we can extract their separation to be
0.137 nm, in agreement with the expectation of 0.136 nm\textsuperscript{107}. From the TEM images it is also possible to determine the value of the $c_{Si}$ lattice parameter using the HAADF intensity profile integrated over the blue rectangular area marked in Fig. 5.3b, obtaining a value of $c_{Si} = 0.634$ nm, not corrected for mutual core/shell strain.

**Figure 5.3.** Atomic-scale imaging of the GaP/Si interface. (a) Aberration-corrected HAADF STEM image of GaP/Si interface obtained in the $[11\bar{2}]_{hcp}$ zone axis. b) Magnified image of the region framed by the red box in (a). c) The structural model constructed based on (a). (d) HAADF intensity profile performed on a Si dumbbell (orange box in (b)) showing that the spatial resolution of the Si dumbbells is 0.1365 nm. From the same profile, we estimate that the Si atomic radius is around 0.110 nm. (e) Intensity profile integrated over the blue rectangular area marked in (b) from which we determine the $c_{Si}$ parameter.

Previous literature claims of the existence of 2$H$ or 9$R$ hexagonal phases in Si do not provide conclusive evidence. In most of these studies, both thin films and NWs were identified to grow in the $\langle 110 \rangle$ or $\langle 112 \rangle$ directions. Such identification of the growth direction is very delicate, because the diffraction pattern, from which the growth direction is typically extracted, can be complicated from issues such as the overlap of different crystalline grains\textsuperscript{18–20}. In particular, for NWs that have grown mostly tilted with respect to the normal to the substrate surface, the determination of the growth direction is not straightforward. In Ref. \textsuperscript{20}, an example is shown where the same NW is imaged in two different zone axes. In one of the zone axes, it seems that the NW grows in the $\langle 1\bar{1}2 \rangle$ direction, while imaged in the other orientation, it seems that it grows in the $\langle 110 \rangle$ direction. Consequently, the crystalline structure seems to be different. Moreover, for these growth directions, assessing the possible existence of the hexagonal phase is problematic, since the appearance of a regular periodicity can arise from either
the overlapping of different crystal grains originated from inclined defects or from regularly distributed SFs. To avoid any misunderstanding and complement the TEM studies, since in TEM images only a projection of the growth direction can be obtained, a complementary study from the SEM images, estimating the angle of the NWs with respect to the substrate surface and therefore estimating the growth direction of the sample, provides crucial information. In addition, we can use this information to tilt the NWs in the appropriate zone axis, so that TEM images exhibit the correct growth direction and consequently the determination of the crystalline structure can be reliably performed.

Figure 5.4. Cross-sectional GaP/Si core/shell. (a) HAADF STEM and EDX overlapped images of a cross-sectional lamella of one representative GaP/Si core/shell NW. Scale bar is 100 nm. (b) Aberration-corrected HAADF image in the [0001] projection of the GaP/Si interface for the region marked with a white square in (a). Scale bar is 5 nm. (c) Magnified images of the regions framed by the blue and red boxes in (b). (d) HAADF intensity profile integrated over the green rectangular area marked in (b).

As opposed to these previous studies, in our case the existence of $2H$ hexagonal Si is not affected by the aforementioned ambiguities since the NWs grow vertically from a GaP (111)$_b$ substrate. Therefore, our measurements will
not be affected from possible overlapping of different grains or from the periodic appearance of SFs, two problems that plagued previous claims of observation of hexagonal Si.

To fully characterize the lattice parameters of this new Si crystal phase in TEM, we prepared a thin lamella to allow analysis in the cross sectional [0001] direction. Fig. 5.4a displays the HAADF STEM and EDX overlapped images of a cross-sectional lamella of a representative GaP/Si core/shell NW, further confirming that the Si shell is uniformly deposited around the six \{11\overline{2}0\} side facets of the GaP core. Fig. 5.4b is an aberration-corrected HAADF image in the [0001] projection of the GaP/Si interface for the region marked with a white square in Fig. 5.4a. The regions marked with red and blue rectangles in Fig. 5.4b are magnified in Fig. 5.4c and illustrate the atomic arrangement characteristic of the hexagonal crystal structure in the [0001] projection. Our results allow a direct determination of the $a_{Si}$ parameter, which turns out to be $a_{Si} = 0.389 \text{ nm}$ (directly observed value, not corrected for mutual core/shell strain). Fig. 5.4d shows the intensity profile integrated over the green rectangular area marked in Fig. 5.4b, from the shell (dark contrast) to the core (bright contrast), where we can identify the transition area with a width of about 1.09 nm, corresponding to four monolayers, the inter-planar distance of \{1\overline{1}00\} being 0.272 nm. This shows that relatively sharp GaP/Si interfaces can be formed.

### 5.3 X-Ray Diffraction

By the use of X-ray diffraction from synchrotron radiation, the lattice parameters can be measured for a large ensemble of NWs. This allows us to obtain a more precise estimate of the $a_{Si}$ and $c_{Si}$ lattice constants. It was confirmed that no intensity occurs around Bragg peak positions of nominal cubic Si. Fig. 5.5a shows a reciprocal space map covering several Bragg peaks as indicated in the plot; Fig. 5.5b is the corresponding line integration.
Figure 5.5. X-ray diffraction. The intensity distribution around a series of Bragg peaks corresponding to the hexagonal phase has been measured using an X-ray energy of 10.3 keV, and a linear X-ray detector to speed up data collection. (a) X-ray diffraction asymmetric reciprocal space map showing the logarithmic scattering intensity along the rod including the $(\overline{2}2\overline{4})$ cubic GaP substrate peak (marked by a white cross). “TW” denotes twinned material occurring only in the NWs, “Sub” denotes the substrate peak and “NW” the hexagonal NW-related peak. The hexagonal Bragg peaks from the NW, which result from the mutually strained hexagonal GaP core and Si shell material, show clear deviations from the GaP peak positions, due to the different lattice parameter of hexagonal Si. (b) X-ray diffraction intensity line integration cut along the $[000\overline{1}]$ direction in the area marked by the white rectangle in (a), showing clearly the presence of the $(10\overline{1}5)$ and $(10\overline{1}\overline{6})$ hexagonal peaks. (c) Plots of the dependence of the values of the $a_{Si}$ and $c_{Si}$ lattice constants for different Si shell thicknesses together with a polynomial fit showing the convergence to the bulk values $a_{Si}$ and $c_{Si}$ for “$a$” and “$c$”, respectively, for increasing shell thickness. We note that the Si shell thickness increases towards the top of the wires, resulting in a relatively large spread in shell thickness.
In order to determine the lattice parameters, we have employed two different analyses. The first one determines the lattice parameters as a function of Si shell thickness from the XRD peak positions and uses a model fit to obtain the strain-corrected (bulk) lattice parameters $a_{Si}$ and $c_{Si}$ of hexagonal Si. The second more elaborate one is based on finite element modeling (FEM) and corroborates the simplified model assumptions of the first approach. This will be discussed in detail in the next paragraph. The result is plotted in Figs. 5.5c and 5.5d as a function of the Si shell thickness. The dots correspond to the measured lattice parameters while the solid line and the shaded area show our model with the fitted results of $a_{Si} = 3.8242 \pm 0.0006$ Å and $c_{Si} = 6.3237 \pm 0.0004$ Å (dashed lines). The shaded area actually depicts the range of curves of our model for the different core thicknesses ($80 – 155$ nm) within the measured sample series, while in the analysis we have used the particular geometrical dimensions of each sample as obtained from the detailed TEM study.

As mentioned, for the determination of the lattice parameters, we have utilized two analyses. Firstly, each peak position of the different Bragg peaks yields a value of $a_{Si}$ and $c_{Si}$. However, since the Si shell is strained by the GaP core material, these values depend on the exact NW geometry and hence the strain state of core and shell. Therefore, we analyze the results for different shell thicknesses: While for the thinnest shells a finite influence of the core can still be expected, for the thicker shells the core has virtually no influence any more, and the values converge towards the true lattice parameters of hexagonal Si, $a_{Si}$ and $c_{Si}$. Since the elastic parameters of Si and GaP differ only by about 10%, we assume that the lattice parameter of the core/shell system is the average between the lattice parameters of hexagonal GaP and the unknown ones of Si, weighted by the volume ratio $V_{core}/V_{total}$ of GaP core and Si shell:

$$a = \frac{V_{core}}{V_{total}} a_{Gap} + \left(1 - \frac{V_{core}}{V_{total}}\right) a_{Si}$$

$$c = \frac{V_{core}}{V_{total}} c_{Gap} + \left(1 - \frac{V_{core}}{V_{total}}\right) c_{Si}$$

This neglects, beside the small difference in elastic properties, the inhomogeneity of strain due to the NW shape. However, these are negligible, as we will show below. To determine the true (i.e. corrected for the small but finite strain in the core/shell system) lattice parameters of hexagonal Si, $a_{Si}$ and $c_{Si}$, we fitted the model to our data, considering the actually slightly different core thicknesses and the statistical errors of geometrical parameters (both within a single NW as well as within the illuminated NW array) as well as the scatter of lattice parameters obtained for all measured Bragg reflections for each shell thickness.
In order to take into account the effect of the mutual strain, we have performed finite element modeling of the NWs using the geometric parameters from SEM and TEM. Therefore, we have run simulations with the $a_{Si}$ and $c_{Si}$ lattice constants of hexagonal Si as free parameters and adjusted them to reproduce the Bragg peak positions in XRD simulations based on the FEM results. The only unknown quantity in this case is the elastic behavior of hexagonal Si, which can be very well estimated from a conversion of the elastic tensor of cubic Si\textsuperscript{108}, and has actually only a very small influence (as for many III-V materials existing in both cubic and hexagonal phases). Due to symmetry (of wire shape and crystal structure), it is sufficient to simulate one quarter of the wire. Further only a 700 nm long segment on top of a cubic GaP substrate was simulated to reduce the computational effort, since the strain is homogeneous along $z$-direction except for a short region close to the substrate. The boundary conditions used in the simulations are the following: nodes within the interface to the substrate are kept fixed, nodes within symmetry interface planes are allowed to move only within those planes, all other faces are free to relax. As initial conditions, the lattice mismatch between the hexagonal GaP core and the hexagonal Si shell with respect to the cubic GaP substrate are set as initial strain values. Upon relaxation of the structure, core and shell tend towards their bulk lattice parameters, keeping the boundary conditions intact. Fig. 5.6 shows the diagonal strain tensor components $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$, respectively.

![Figure 5.6. FEM simulations of the strain distribution. Diagonal strain tensor components $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$.](image)

As can be seen, the two in-plane components $\varepsilon_{xx}$ and $\varepsilon_{yy}$ are almost identical except for the interchange of $x$ and $y$ direction and small differences, since the
NW shape is not symmetric with respect to exchanging \( x \) and \( y \). The displayed strains are with respect to the bulk material of core and shell, respectively. It can be seen that the strain is almost constant inside core and shell, apart from a small region close to the substrate, and very small regions close to the edges. Those regions contribute virtually nothing to the scattering signal. The absolute difference of strain between core and shell is virtually identical to the lattice mismatch, \( \text{i.e.} \) the lattice parameters of core and shell are virtually identical. The same is true for the strain component along growth direction (crystalline c-axis) \( \varepsilon_{zz} \), where the strain values are smaller due to a smaller lattice mismatch between core and shell. Overall the FEM simulations, which consider the small differences in elastic parameters between core and shell as well as the crystalline anisotropy of the elastic parameters as well as the hexagonal shape of the NWs, show that the assumption of constant volume-averaged lattice parameters used in the data evaluation is well justified. The resulting values for \( a_\text{Si} \) and \( c_\text{Si} \) from the more sophisticated FEM analysis turn out to be equivalent to the ones from our model within the error bars of the analysis.

### 5.4 Raman Spectroscopy Studies

A fingerprint of the crystal symmetry can also be obtained by probing the phonon modes by Raman spectroscopy. Cubic Si belongs to the \( O_h^7 \) (Schönflies notation) space group and exhibits one triply degenerate optical phonon mode at the zone center with \( F_{2g} \) symmetry at \( 521 \, \text{cm}^{-1} \), recognizable in the dashed spectra in the lower panel of Fig. 5.7a. Hexagonal Si belongs to the \( D_{6h}^4 \) space group and is expected to have three Raman active modes with \( A_{1g}, E_{1g} \) and \( E_{2g} \) symmetries\(^{109}\). The nondegenerate \( A_{1g} \) is the longitudinal optical (LO) mode and the doubly degenerate \( E_{1g} \) and \( E_{2g} \) are transversal optical (TO) modes.

We performed Raman spectroscopy measurements on single NWs, with a Si shell between 20 and 40 nm, which are transferred on a TEM grid placed on a diamond surface. Spectra were collected under the four main polarization configurations, i.e. with the polarization of the excitation/scattered radiation being parallel/perpendicular to the NW growth axis (Fig. 5.7a, upper panel). All Raman spectra collected from hexagonal Si exhibit a phonon mode at \( 496 \, \text{cm}^{-1} \) and a mode at \( 514 \, \text{cm}^{-1} \). The mode at \( 496 \, \text{cm}^{-1} \) arises from backfolding of the TO phonon dispersion of the cubic structure from the \( \Gamma \) to the L point\(^{110}\), resulting in a mode with \( E_{2g} \) symmetry\(^{17,109}\). The mode at \( 514 \, \text{cm}^{-1} \) has \( A_{1g} \) symmetry and originates from the splitting of the triply degenerate \( F_{2g} \) mode of the cubic phase into \( A_{1g} \) and \( E_{1g} \) modes due to the reduced symmetry of the hexagonal phase\(^{111,112}\). If the phonon propagation direction is parallel to a crystallographic axis, only phonons polarized parallel (\( A_{1g} \)) or perpendicular (\( E_{1g} \)) to the optical axis, corresponding in our case to the growth direction, are
observed\textsuperscript{112}. Therefore, in crystals with the hexagonal crystal phase the $A_{1g} - E_{1g}$ splitting occurs. Here, we do not observe the mode with $E_{1g}$ symmetry because it is the mode mostly affected by the shell thickness since it has polarization perpendicular to the NW growth direction. Furthermore, the full

**Figure 5.7.** Raman scattering. (a) Upper panel: Polarized Raman spectra obtained from a single hexagonal GaP/Si NW (120 nm shell) in $x(z,z)x$, $x(y,y)x$, and $x(z,y)x$ scattering configurations as black, red, and green spheres, respectively. For the notation of the scattering configuration see Ref.\textsuperscript{110}. Lower panel: Spectra collected from Si (100) bulk in $x(z,z)x$ and $x(y,y)x$ scattering configurations are plotted as black and red dashed lines, respectively, as reference. All spectra have been normalized and shifted vertically for clarity. (b) Raman spectrum of an ensemble of hexagonal GaP/Si NWs (170 nm shell) collected while increasing pressure from 0 GPa (black solid line) up to 9 GPa (red solid line), and then decreasing the pressure again to 0 GPa (grey solid line). The spectra have been normalized and shifted vertically for clarity. The spectra have been collected tentatively always from the same bundle of NWs.

because it is the mode mostly affected by the shell thickness since it has polarization perpendicular to the NW growth direction. Furthermore, the full
width at half maximum (FWHM) of the modes is ranging from 3 to 4 \text{ cm}^{-1},
indicating the excellent crystal quality of the NWs.

In order to investigate the stability of the crystal structure, we performed high pressure Raman experiments on NW bundles with 170 nm hexagonal Si shell. We have plotted the spectra collected at 0 GPa (black solid line), 9 GPa (red solid line) and at 0 GPa after releasing the pressure (grey solid line) in Fig. 5.7b. In this case, besides the peaks described above, we observe also a mode at 520 cm\(^{-1}\) which arises from the defected region on the top part of the NWs. Comparing the spectra collected at 0 GPa and 9 GPa, two main features can be observed:

i. The frequency shift of the phonon modes due to a variation of the interatomic distance.

ii. The modification of the line shape, \textit{i.e.} a change in the FWHM of the modes, due to anharmonic interactions affecting phonon lifetime.

![Figure 5.8](image)

**Figure 5.8.** Spatially resolved Raman measurements. Spectra collected under the \(x(z,z)\textit{x}, x(y,y)\textit{x}, \text{ and } x(z,y)\textit{x}\) scattering configurations as black, red, and green spheres, respectively, from the defected top part (top panel) and the defect free middle part (bottom panel) of the NW.

As has been previously discussed, the top part of the NWs exhibits a defected structure. In order to address the effect of these defects on the Raman spectra,
we performed spatially resolved Raman measurements along the NW axis. In Fig. 5.8 we report spectra collected from the defected top part and from the defect free middle of the NW, in the top and bottom panel, respectively.

The Raman spectra collected from defect-free part of the NW exhibit the $E_{2g}$ phonon mode at $496\; cm^{-1}$ and the $A_{1g}$ mode at $514\; cm^{-1}$, typical of hexagonal Si, as discussed in the main text. The spectra collected from the defected top part of the NW are instead dominated by a peak at $520\; cm^{-1}$, which corresponds to the triply degenerate $F_{2g}$ mode of the cubic phase.

We did not observe any structural phase transition even up to $9\; GPa$, which would be manifested in abrupt modification of the pattern of Raman peaks observed (i.e. appearance or disappearance of phonon peaks and new spectral features in the Raman spectra). As further proof, we collected a measurement after the release of the pressure down to $0\; GPa$ (Fig. 5.7b, grey solid line). The Raman spectrum fully recovers its original characteristics in terms of frequencies and full width at half maximum (FWHM) of the phonon modes. This is a clear indication of the high stability of the hexagonal crystal phase up to $9\; GPa$.

Our approach of crystal structure transfer enables the fabrication of pure and stable hexagonal Silicon, which properties can now be assessed. This generic method opens a route to synthesize a new class of semiconductors consisting of hexagonal group IV materials. Next challenge is to demonstrate hexagonal Ge and SiGe compounds, which are expected to have a direct optical band gap and are compatible with Si technology. Moreover, the exceptional control of crystal structure and the ability to make crystal phase junctions, which has been unique so far to III-V NWs can now be transferred to the group IV semiconductors opening new routes for band structure engineering of the technologically most important semiconductors.
Chapter 6 - Single-Crystalline Hexagonal Silicon-Germanium

Group IV materials with the hexagonal diamond crystal structure have been predicted to exhibit promising optical and electronic properties. In particular, hexagonal Si\(_{1-x}\)Ge\(_x\) should be characterized by a tunable direct band gap, with implications ranging from Si-based light-emitting diodes to lasers and quantum dots for single photon emitters. Here we demonstrate the feasibility of high-quality defect-free and wafer-scale hexagonal Si\(_{1-x}\)Ge\(_x\) growth with precise control of the alloy composition and layer thickness. This is achieved by transferring the hexagonal phase from a GaP/Si core/shell nanowire template, the same method successfully employed by us to realize hexagonal Si. We determine the optimal growth conditions in order to achieve single-crystalline layer-by-layer Si\(_{1-x}\)Ge\(_x\) growth in the preferred stoichiometry region. Our results pave the way for exploiting the novel properties of hexagonal Si\(_{1-x}\)Ge\(_x\) alloys in technological applications.

6.1 Introduction

Si with the diamond cubic crystal structure is the most widely used technological semiconductor. Unfortunately it lacks in its optical properties, since in this crystal phase it exhibits an indirect band gap.\(^{34,36,37}\) The integration of an element displaying efficient light interaction with Si technology is of high technological interest. Unfortunately, III-V materials that display this behavior have lattice mismatch issues with Si. Ge, a group-IV semiconductor like Si, with the diamond cubic crystal structure also exhibits an indirect band gap. Interestingly, Ge with the hexagonal diamond crystal structure is predicted to present a direct band gap of 0.3 eV, which corresponds to a wavelength of 4.1 μm in the infrared, predicted by the empirical pseudopotential method with spin-orbit interactions.\(^{33}\) Other studies have also been carried out which use first-principles calculations\(^{36}\) and empirical pseudopotential method without spin-orbit interactions\(^{37}\). By combining hexagonal Si\(^{11-13,15-17,22,74,113-118}\) and Ge\(^{119,120}\) to form an alloy with the hexagonal diamond structure, it should be possible to engineer the band structure in such a way that the direct band gap of the Si\(_{1-x}\)Ge\(_x\) alloy shifts to higher energies.\(^{33,36,37,121}\) Based on the predicted band structure of hexagonal Si and Ge, Si\(_{0.35}\)Ge\(_{0.65}\) could present a direct band gap in the region of 1.7 μm, which is close to the telecommunication wavelength of 1.5 μm. In addition, the lattice mismatch between the Si\(_{1-x}\)Ge\(_x\) alloy for \(x < 1\) and a Si substrate is reduced with respect to that between pure Si and pure Ge. In the literature, band gap engineering with Si\(_{1-x}\)Ge\(_x\) alloys has been explored by calculation of the electronic structure of cubic Si\(_{1-x}\)Ge\(_x\) alloys\(^{122-125}\) and
specifically growth of a cubic Ge/SiGe core/shell NW system has been published.\textsuperscript{126,127}

Here, we present the growth of hexagonal Si\textsubscript{1-x}Ge\textsubscript{x} throughout the whole range of stoichiometry. We utilize a novel combination between III-V and group-IV materials by using wafer-scale arrays of non-tapered and single-crystalline hexagonal GaP/Si core/shell NWs as templates\textsuperscript{22} and overgrow them with a second epitaxial SiGe shell using MOVPE. As a result, we obtain GaP/Si/SiGe core/multi-shell NWs. We expect that the strain stemming from the lattice mismatch between the inner Si and the outer SiGe shell can be accommodated to some extent by the NW geometry, as has been reported for Ge/Si core-shell NWs\textsuperscript{81} thus contributing to achieve high shell Ge content without introducing dislocations. The growth was carried out on nanoimprinted substrates, to provide a high number of NWs -on the wafer scale- and consistency. In Ref.\textsuperscript{21} we explored different temperatures and provided details on the growth conditions and kinetics in order to present high quality single-crystalline hexagonal GaP/Si core-shell systems\textsuperscript{22}. These acted as a springboard in order to achieve the new growths presented in this work.

### 6.2 Growth

In Fig. 6.1a we present a SEM image with an array of about 7 µm long GaP/Si/SiGe core/multi-shell NWs. The cross-sectional SEM image at a higher magnification (inset of Fig. 6.1a) shows that the NWs are non-tapered with smooth sidewalls. The growth of the defect-free GaP/Si core/shell NWs with the hexagonal diamond crystal structure has been described in Ch.5.\textsuperscript{22} In this case though, the Si shell thickness was kept to a minimum of 10-12 nm. This could potentially act as sacrificial buffer layer to trap any P or Ga species from the GaP core from diffusing into the SiGe shell. Directly after the growth of the Si shell and in the same growth run, the SiGe shell was grown. This was done by switching off the Si\textsubscript{2}H\textsubscript{6} precursor gas and gradually lowering the temperature of the MOVPE growth chamber to either 600 °C or 700 °C. Once the aimed temperature was reached and stabilized, Si\textsubscript{2}H\textsubscript{6} and GeH\textsubscript{4} were introduced to the chamber and their flows were adjusted to suit the desired stoichiometry. Si\textsubscript{2}H\textsubscript{6} molar flow was modified from $2.87 \times 10^{-7}$ at the low end, to $1.00 \times 10^{-4}$ at the high end, while GeH\textsubscript{4} from $3.66 \times 10^{-6}$ at the low end, to $3.33 \times 10^{-4}$ at the high end, in order to achieve the desired ratio. H\textsubscript{2} was used as a carrier gas for the precursors and the total flow into the rector was 8.2 l/min. At the end of the SiGe shell growth, the precursor flows were terminated, the heating elements switched off and the chamber allowed to cool down to room temperature.
Figure 6.1. Hexagonal GaP/Si/SiGe core/multi-shell NWs. (a) SEM image with NW morphology overview of a representative sample (tilt angle 30° normal to substrate). The inset shows a cross-sectional SEM image of the same sample; (b) Low-resolution HAADF STEM image of a representative NW; (c) HAADF HRSTEM image of the SiGe/Si/GaP interfaces viewed in the [11-20] zone axis and the corresponding FFT as inset; (d) EDX map of the NW in (b). The various elements are color-coded to elucidate the structure, green for GaP, red for Si and blue for Ge; (e) Compositional line profile crossing the structure, averaged over the width of the white dotted rectangle in (d).

6.3 Structural/Chemical Characterization

Fig. 6.1b displays a HAADF STEM image of a representative GaP/Si/SiGe core/multi-shell NW where the SiGe shell has been deposited at 600 °C. The HAADF high-resolution STEM image of the SiGe/Si/GaP interfaces (Fig. 6.1c) viewed in the [11-20] zone axis together with the FFT (see inset) reveal the hexagonal phase character of the system, as well as the perfect epitaxy between the layers. The composition of the GaP/Si/SiGe core/multi-shell NWs is confirmed from the EDX map (Fig. 6.1d) and the compositional line profile (Fig. 6.1e) extracted from the map. For this NW the Ge content measured in terms of at.%, is found to be 60.0 ± 0.5 at.% in the outer shell.
6.4 Cross-sectional Studies

To improve our understanding of the vapor-solid shell growth mechanism as well as for future optical characterization experiments it is important to assess the homogeneity of the Ge distribution along the entire shell. We therefore determine the Ge content in the SiGe shell of the samples grown. To quantify the Ge content, the samples were prepared by focused ion beam (FIB) by thinning the NWs in the radial direction down to around 60-80 nm to facilitate cross-

![Cross-sectional TEM image](image)

**Figure 6.2.** Cross-sectional study of GaP/Si/SiGe core/multi-shell NWs. (a) Bright Field TEM cross-sectional image of a representative NW; (b) the corresponding FFT to (a); (c) EDX chemical analysis of the same cross-section, where the Ge content in each facet has been averaged and the results in each facet are indicated by different symbols. The color-coding follows the same scheme as in Figs. 6.1d and 6.1e.

sectional TEM studies. In Fig. 6.2a, a cross-sectional BFTEM image is shown. The cross-section has been aligned along the [0001] direction. The hexagonal
symmetry of the six \{1-100\} facets of the SiGe shell around the Si shell and GaP core is evident (Fig. 6.2b). The Ge content has been evaluated averaging over positions from each of the six facets, each represented by different symbols in Fig. 6.2c. From this analysis, we indeed find that the Ge content is uniformly distributed in the SiGe shell, in this specific case being around 60.0 \(\pm\) 0.5 at.%.

### 6.5 Ge Incorporation

To further reveal the SiGe shell growth mechanism, it is useful to plot the resulting incorporated Ge content in the shell, as determined by EDX spectroscopy, as a function of the Ge content in the precursor gas flow in the MOVPE chamber, for all the heterostructures investigated. This is shown in Fig. 6.3.

**Figure 6.3.** Ge incorporation into the SiGe shell and growth modes. (a) at.% Ge content incorporated into the SiGe shell, as determined by EDX spectroscopy, as a function of the at.% Ge content in the precursor gas mixture in the MOVPE chamber; (b), (c) and (d) HAADF STEM image of a sample grown at: 600 °C at a Ge content 60 at.% input; 67 at.% incorporated exhibiting F-M growth, 700 °C at 80 at.% input; 66 at.% incorporated exhibiting S-K growth and 700 °C at 99 at.% input; 91 at.% incorporated exhibiting V-W growth, respectively.
where we observe a higher incorporation of Ge at the lower deposition temperature of 600 °C as compared to the one performed at the higher temperature of 700 °C. The fact that the Ge content of the SiGe shell, for the same amount of input Ge (in the vapor phase in the precursor gas mixture) during MOVPE growth, is higher at lower temperatures can be understood as follows. The two precursor gasses, namely Si$_2$H$_6$ and GeH$_4$, have different decomposition temperatures, around 640 °C for Si$_2$H$_6$ and around 300 °C for GeH$_4$. This means that at 600 °C, the Si$_2$H$_6$ has not been completely thermally decomposed, and therefore the relative amount of Ge available that can be incorporated into the shell is higher. The net result is that at 600 °C the ratio of Ge in the SiGe shell is higher than in the precursor gas mixture. On the other hand, at 700 °C more Si$_2$H$_6$ has decomposed, thus more Si is available for deposition and the relative amount of Ge incorporated into the shell decreases.

### 6.6 Growth Modes

A characteristic feature of the cubic Si/SiGe system is the appearance of different growth modes as the Ge content, and consequently the lattice strain, increases in the SiGe shell and we observe it for the hexagonal phase as well. For most of the samples (for a Ge content of less than 80 at.% grown at 600 °C and of less than 60 at.% grown at 700 °C, indicated by solid symbols in Fig. 6.3a), uniform layers are formed suggesting a Frank-van der Merwe (F-M) layer-by-layer growth mode. Furthermore, all the samples grown at 600 °C up to the Ge content of 80 at.%, are defect-free. As can be observed in Figs. 6.3a and 6.3c, the samples grown at 700 °C at a Ge content above 60 at.% exhibit a thin SiGe layer combined with the formation of islands. For high Ge content, the strain build-up after a few layers of layer-by-layer growth leads to strain relaxation by transitioning into island growth. This morphology is characteristic of the well-known Stranski-Krastanov (S-K) growth mode. The sample grown at 600 °C with 80 at.% Ge, which is the point where the transition from F-M to S-K growth mode takes place, is the exact point where defects start to appear, while all the samples below that are defect-free. Moreover, for the growths at 700 °C, when the Ge content is above 90 at.%, the SiGe shell is characterized in most cases by island growth only, therefore being dominated by the Volmer-Weber (V-W) growth mode (Figs. 6.3a and 6.3d). We note here that the islands (Figs. 6.3c and 6.3d) do not seem to exhibit the typical pyramid or dome shape observed in heterostructures with the cubic crystal structure. Since the shape of the island structures formed during S-K and V-W growth depends on the surface energies, one would not expect that the same shapes would appear for the hexagonal crystal structure or for growth on a NW sidewall. On the other hand, we observe that for the growths carried out at 600 °C, the layer-by-layer growth continues up to a Ge content of 80 at.% (Figs. 6.3a and 6.3b). This difference in morphology
can be understood in terms of the combination of strain and different diffusion lengths of the adatoms for the different growth temperatures, which has been elaborated for metastable layers of cubic SiGe. In particular, strain increases with the Ge content in the shell and at high temperatures the adatom diffusion length is longer. Thus, adatoms can diffuse over longer distances to relieve strain by forming islands. On the other hand, at lower temperatures the adatom diffusion length is shorter, thus the adatom diffusivity is too short to form islands in the time frame available for growth. As a result, a continuous metastable layer with increasing strain is grown. In summary, from Fig. 6.3 we observe that at the growth temperature of 600 °C not only is the Ge incorporation more efficient, but also that layer-by-layer defect-free growth continues up to higher Ge contents, well above the expected direct band gap transition stoichiometry of about Si$_{0.35}$Ge$_{0.65}$.

### 6.7 Kinetics

The growth kinetics have been studied in more detail, and especially the growth rate as a function of time and temperature. The linear dependence of the SiGe thickness with respect to the growth time indicates that the growth rate is roughly constant (Fig. 6.4a). This indicates that the growth rate limiting step is determined by surface kinetics rather than by e.g. volume diffusion. The growth rate depends however on the Ge content. For the growths performed at 600 °C, the shell thickness at 22 min of growth is approximately independent of the Ge content. For longer growth times the growth rates start to differ; in particular the growth rate for the samples with a Ge content in the range of 11-13 at.% is markedly smaller than for the ones with a Ge content in the range of 27-33 at.% and 43-49 at.% (for which instead the rate is almost the same). This is indicated by a smaller slope for the 11-13 at.% Ge samples, and hence results in a thinner shell, for reasons that we discuss below. For the growths at 700 °C, the thickness doubles for the region of 27-33 at.% Ge relative to the same at.% Ge region at 600 °C.

In addition, the study of the growth rate was performed with a series of samples grown for the whole range of SiGe stoichiometry and for the two different temperatures of 600 °C and 700 °C. In Fig. 6.4b we present the growth rate as a function of the Ge content for the two deposition temperatures of the SiGe shell. In terms of the Ge content, two well-differentiated regimes can be observed. First of all, a regime of low Ge content, characterized by a marked increase of the growth rate as the Ge content is increased. In this regime, strain does not influence the growth dynamics, and instead the increase in growth rate can be attributed to an increase in hydrogen desorption from the growth surface due to Ge. Indeed, Ge acts to lower the activation energy of hydrogen desorption, thus freeing-up more surface sites for Si and Ge growth species. This
results in an increase in the growth rate with increasing Ge content. The second regime is found in the region with a high Ge content, characterized by a decrease of the growth rate as a function of Ge content. Two different reasons have been proposed to explain this behaviour; either high strain$^{135-137}$ and/or decreased reactive hydride adsorption.$^{134}$ In the first case, strain starts to play the dominant role, and the decrease in the growth rate that takes place is attributed to strain accumulation due to the very high Ge content. Note that as the lattice constant is increased, so does the diffusion energy barrier, and this makes

Figure 6.4. SiGe shell growth kinetics. (a) SiGe shell thickness as a function of growth time for various regions of Ge content, where a linear trend is observed. For the SiGe shells grown at 600 °C at a Ge content in the range of 27-33 at.% and 43-49 at.% the thickness is the same; (b) SiGe shell growth rate as a function of the Ge content of the shell. The growth rate was defined only for F-M growth so all the points in the 600 °C curve represent smooth layer growth. On the other hand, the 700 °C curve exhibits the initial increase, but the subsequent decrease is quickly cut off due to the onset of S-K growth.
diffusion more difficult. In turn, less diffusion implies a lower growth rate. The second reason for the decreasing growth rate at high Ge content is a decreased reactive hydride adsorption. This has been explained by a lower adsorption coefficient of the precursors, resulting in a lower growth rate. The competition between these different effects is clearly seen in Fig. 6.4b, and is in agreement with previous studies. While the dependence of the growth rate with the Ge content of the shell shows the same trend for the two temperatures studies, 600 °C and 700 °C, the quantitative behavior is different. In the case of the growth at high temperature (700 °C), we find that the peak growth rate is higher, and reached for a smaller Ge content than for the growth at low temperatures (600 °C). This behavior can be understood in terms of adsorption and desorption, by a similar mechanism as that discussed above. Indeed, for higher temperatures, besides the decomposition of the precursors both the adatom diffusion and the hydrogen desorption increase, explaining the markedly higher peak growth rates for the shells grown at 700 °C. Furthermore, the 700 °C curve gets cut off relatively quickly due to the onset of S-K growth. In essence, Fig. 6.4b further solidifies the claim that for the growth at 600 °C, layer-by-layer defect-free growth continues up to higher Ge contents, above Si$_{0.35}$Ge$_{0.65}$ where the direct band gap transition is expected to occur.

In conclusion, in this work we have presented the growth of single-crystalline defect-free SiGe with the hexagonal diamond crystal structure. We have reported how the growth temperature can lead to striking differences in the resulting SiGe layer morphology: SiGe layers grown at lower temperatures exhibit uniform layer-by-layer F-M growth, while at higher temperatures and for the same Ge content, island-based S-K growth dominates. The maximum stoichiometry achieved for defect-free smooth layer thin film growth was at 77 at.% Ge, significantly above the predicted direct band-gap transition at 65 at.% Ge. Moreover, we observe that layer growth continues to this high value significantly more at the growth temperature of 600 °C. Our results pave the way for the utilization of hexagonal SiGe in optoelectronic applications, and in this respect, additional studies should be performed for the detailed characterization of the optical properties of this new material.
Chapter 7 – Single-Crystalline Hexagonal Si and SiGe Nanowires

The fabrication of Si with the hexagonal diamond crystal structure has long been a goal, since it holds the promise of novel optical properties along with silicon technology compatibility. A hexagonal SiGe alloy has recently been proposed for the same reasons but with the major addition of being expected to be a fully direct band gap semiconductor. Since the hexagonal crystal structure has been observed to appear frequently in nanowires, the first approach has been to grow hexagonal silicon nanowires. Unfortunately, defects have plagued these attempts. Another approach has been to utilize a hexagonal substrate and grow hexagonal Si and SiGe epitaxially as a shell around a nanowire core. The ideal solution though, would be to grow defect-free hexagonal Si and SiGe structures with as big a volume as possible in order to observe the optical properties, and where the possible detrimental diffusion of dopants from the supporting structure is minimized. Here, we present the growth of defect-free and wafer-scale hexagonal Si and SiGe nanowires. We confirm the absence of defects by transmission electron microscopy both in the lateral and cross-sectional directions and show the growth of the nanowires through the whole range of stoichiometry from Si to Ge. We further showcase that Si and SiGe segments can co-exist simultaneously without defects in a single heterostructure nanowire. With this, we show that even more complex Si and SiGe structures are possible by exploring the third dimension in epitaxial nanowire growth and pave the way for studying the promising optical properties.

7.1 Introduction

Combining the strengths of photonics and electronics in a single material would yield a powerful platform. However, bulk Si and Ge, that normally crystallize in the diamond cubic crystal structure, have an indirect band gap severely limiting their applications in the optical domain. There have been several attempts to engineer a solution to this problem and obtain light emission, such as intrinsic and alloy-induced luminescence, radiatively active impurities, Si/Ge superlattices and quantum confined structures. The main issue here is the practicality of the solutions due to the decrease in emission with increasing temperature. Even though they do allow light emission, they are not necessarily practical and it may not be possible to use these effects in the production of practical devices especially with efficient optical emission at room temperature. Interestingly, it has been predicted that Ge in the hexagonal diamond crystal phase will exhibit a small direct band gap of around 0.3 eV (equivalent to 4.1 μm wavelength), while hexagonal Si is expected to have a
minimum in the conduction band at the \( \Gamma \)-point, although still being indirect\(^{34,36,37,121} \). It could be possible, based on these predictions, to obtain a direct band gap material by alloying hexagonal Si\(^{11-13,15-17,22,74,113-118} \) and Ge\(^{119,120} \) in order to fabricate hexagonal Si\(_{1-x}\)Ge\(_x\)\(^{138} \). The hypothesized direct band gap of about 1.7 \( \mu \)m should present itself around the \( \text{Si}_{0.35}\text{Ge}_{0.65} \) composition, corresponding to an emission wavelength close to the telecommunications wavelength of 1.55 \( \mu \)m (0.8 eV).

In one approach, domains of hexagonal Si and hexagonal Ge were reported; they were formed in cubic phase NWs by a mechanical strain envelope.\(^{113} \) Although the hexagonal phase has been clearly demonstrated this process has limited control and so far, only produces small domains of the hexagonal phase. Recently, the realization of single-crystalline hexagonal Si has been reported in a NW core/shell geometry\(^{22} \). Furthermore, single-crystalline hexagonal SiGe has also been reported using the same geometry with full control of the stoichiometry.\(^{138} \) In that case, the hexagonal SiGe was fabricated as a shell layer of a certain thickness, but ultimate thickness limits to the extent of continuous layer-by-layer growth are imposed by strain accumulation. After some thickness, growth mode transition from layer-by-layer to layer-plus-island and then to pure island growth will take place. The ability to grow a defect-free hexagonal crystal with as much volume as possible is desired for increasing the signals in optical and other measurements. Another issue with this approach may the diffusion of atoms from the GaP crystal template wire into the SiGe shell during the growth of the shell, which occurs at relatively high temperatures. Ga and P atoms are dopants for the group IV semiconductor and will affect the optical properties. So, the quest for a hexagonal SiGe crystal where the critical parameters – crystal purity, extensive volume, impurity absence and the ability to separate completely the crystal from the supporting structure – may be tuned as desired is justified, but also poses another challenge in terms of growth.

In this work, we report a generic scheme for the fabrication of single-crystalline hexagonal Si\(_{1-x}\)Ge\(_x\) NWs with full compositional control by MOVPE. We utilize the crystal structure transfer method\(^{74} \), which we employed successfully in the past to make hexagonal Si\(^{22} \) and Si\(_{1-x}\)Ge\(_x\) shells.\(^{138} \) In this case, we add an additional step by depositing Au particles on the sidewalls of hexagonal NWs and commence Vapor-Liquid-Solid (VLS) growth of NWs, which resemble branches growing out of a tree trunk.\(^{139} \) This enforces the SiGe branches to grow in the hexagonal phase and an arbitrarily long NW can be produced. We first present the growth method for hexagonal Si branch NWs and subsequently the tuning of the Si-to-Ge ratio for Si\(_{1-x}\)Ge\(_x\) branches. Finally, we show the growth of a Si/SiGe heterostructure.
7.2 Branch Fabrication/Growth

In Fig. 7.1a the principle of the process is shown. Initially, vertical hexagonal GaP NW trunks were grown from an array of Au islands defined by nanoinprint lithography.\textsuperscript{60} From XRD and TEM studies we know that the GaP NWs have the hexagonal crystal structure and are basically free of defects (<1 μm\textsuperscript{-1}). On the \{11-20\} side facets a second generation of Au catalyst particles was deposited by thermal evaporation. The side facets were then utilized as a substrate in order to epitaxially grow hexagonal Si branches.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_1.png}
\caption{Growth of hexagonal SiGe NW branches. (a) Branch fabrication by deposition of a Au layer on the sidewall of WZ GaP NW trunks followed by Au droplet formation through annealing and finally, VLS growth of branches by precursor introduction; (b) top-view SEM image of the branches; (c) side-view TEM image of the branches grown on the trunk.}
\end{figure}

In Fig. 7.1b a top-view SEM image is shown of the sample after growth of the branches. The branches grow out in six equivalent <1-100> azimuthal directions. In Fig. 7.1c an overview TEM image is shown, in which the trunk and short branches are clearly visible. From this image, it is clear that all branches grow perpendicular to the long axis of the trunk. On the tip of the branches the Au
catalyst particles are also visible. Imaging along this zone axis should make stacking faults visible; clearly, there are no SF present in the overview TEM image, revealing the high crystal quality of the sample.

### 7.3 Structural Characterization

The structural characterization of the branches and their epitaxial relation to the trunk is presented in more detail in Fig. 7.2.

**Figure 7.2. Structural characterization of branches.** (a) HRTEM image of a defect-free hexagonal branch; (b) magnified views of the NW in (a). The colored rectangles are stitched together from the corresponding rectangles in (a); (c) HRSTEM of the part depicted with a blue rectangle in (b). The hexagonal core of the branch NW and the cubic shell are evident; (d) HRSTEM of the part depicted with a red rectangle in (b). Just below the catalyst particle, no shell growth is present, only the hexagonal branch; (e,f) FFT patterns of the hexagonal branch and the cubic shell from panel (c), displaying the $<11\overline{2}0>$ and the $<110>$ zone axes respectively.

The HRTEM image in Fig. 7.2a, taken along the $<11\overline{2}0>$ zone axis, shows a tapered hexagonal Si branch. HRTEM images at even higher magnification have been produced in order to show the hexagonal layers and are presented in Fig. 7.2b. The core of the branch, which was grown by the VLS mechanism, displays a pure hexagonal diamond crystal structure without planar defects. Branched NW
structures have been reported before, but have not yielded such pure crystal phase branches.\textsuperscript{139,140} In Fig. 7.2c, a High-Resolution Scanning TEM (HRSTEM) is shown, which is a magnified view of the blue rectangle in Fig. 7.2b. The ABABAB... stacking of the hexagonal structure planes in this part is clearly visible (lower part of Fig. 7.2c). The FFT taken from the hexagonal part (Fig. 7.2e) confirms that the branch displays the hexagonal diamond crystal structure. Also from Fig. 7.2c, it is found that the tapering observed is due to simultaneous vapor-solid (VS) shell growth on the \{0001\} side facets of the branch (upper part of Fig. 7.2c). This shell displays the diamond cubic crystal structure and is energetically favored in this direction. In this case, the ABCABC... stacking of the cubic planes is visible. The FFT taken from the cubic part (Fig. 7.2f) confirms that the shell displays the diamond cubic crystal structure. The fact that the cubic shell is due to VS growth is further strengthened by Fig. 7.2d; here we can see that close to the Au catalyst particle there is no cubic shell growth but only hexagonal. Crystal defects are recognizable close to the base of the branch (Fig. 7.2b), at the point where the cubic layers of the shell of the branch, originating from the branch side facet, meet the hexagonal layers of the trunk. This implies that this shell growth originates from nucleation of new layers on the \{0001\} side facets themselves, rather than by extending layers from the hexagonal trunk. Furthermore, the fact that there is no cubic shell growth close to the Au catalyst particle, that the diameter of the hexagonal part just below the catalyst is equal to the initial diameter of the branch and that this core part displays the hexagonal structure, all solidify the claim that the purely VLS-grown NW branch has grown with the hexagonal crystal structure.

**Figure 7.3. Cross-sectional structural characterization of branches.** (a) Cross-sectional HRTEM image of a branch taken along the \(<1-100>\) zone axis; (d) schematic representation of the branch cross-section showing the hexagonal VLS-grown NW along with the cubic shell.

To substantiate the single-crystalline nature of the hexagonal branches, we have prepared cross-sectional cuts of the branches using a Focused Ion Beam
(FIB). In Fig. 7.3a a HAADF STEM image of a cross-section of a branch is presented, showing the crystal morphology. The cross-sectional shape of the branches is rectangular, while the core of the branch displays \{11-20\} and \{0001\} side facets and extends fully to the \{11-20\} side facets, while in the [0001] direction the cubic shell of the branches grows on the \{0001\} facets of the branch core. Note that viewing along the \langle 1-100 \rangle zone axis, there’s no discrimination between the cubic and hexagonal structures, i.e. they look exactly the same. On the other hand, one can easily discriminate between the two structures in the \{11-20\} direction (Fig. 7.2c).

### 7.4 Chemical Characterization

By developing a route for the growth of defect-free hexagonal Si NWs, we have laid the groundwork to further investigate the growth of hexagonal SiGe compound NWs up to pure hexagonal Ge NWs. This is motivated by the expectation that hexagonal SiGe crystals from around a Ge content of Si$_{0.35}$Ge$_{0.65}$ and upwards should exhibit a direct band gap. In Fig. 7.4, we present Energy-Dispersive X-ray (EDX) spectroscopy maps to elucidate the elemental composition of a SiGe branch.

In this case, we measure a composition of Si$_{0.5}$Ge$_{0.5}$ (Fig. 7.4a). The map further clarifies that the composition is uniform along the axis of the branch NW. Cross-sections of the branches were also investigated with EDX, in order to see the composition in the viewing direction which is parallel to the branch axis. The cross-sectional EDX maps (Fig. 7.4b) show that the composition of the branches in their center is uniform, whereas there is an apparent enrichment of Si in the outer shell, with a further Ge enrichment just below the surface. It has been suggested that this segregation is due to preferential oxidation of Si atoms instead of Ge at the surface.$^{141,142}$ This leads to rejection of Ge atoms that are subsequently piled-up at the interface between the Si-oxide and the remaining SiGe layer, essentially creating a Ge-enriched sub-surface layer. However, the formation of a Si$_O$ surface layer that eliminates dangling bonds is probably beneficial for the optoelectronic properties of the branch NWs. With our fabrication methodology, we were able to tune the composition of the hexagonal $Si_{1-x}Ge_x$ branch NWs in the full $0 < x < 1$ range. In Fig. 7.4c, we have plotted the Ge content incorporated into the SiGe branch NW, as determined by EDX spectroscopy, as a function of the Ge content in the precursor gas mixture in the MOVPE chamber. From this, we observe a linear incorporation of the growth species into the branch NW via the VLS mechanism mediated by Au particles. We thusly demonstrate that even defect-free hexagonal SiGe NWs can be grown.
Figure 7.4. Compositional characterization of branches. (a) Composite EDX map of a branch along with the elemental EDX maps; (b) cross-sectional EDX map of a branch along with the elemental EDX maps; (c) solid state Ge branch concentration (obtained by EDX) as a function of gas-phase Ge atomic fraction.
7.5 Heterostructures

The flexibility that this fabrication method provides is evident when aiming to produce even more complex structures. For example, by growing an abrupt junction between a direct and an indirect band gap material, we can confine the carriers and increase optical efficiency. Based on this, we have grown hexagonal SiGe heterostructures along the axial direction of the same branch NW. In Fig. 7.5a, we present a HAADF STEM image of a hexagonal Si$_{0.5}$Ge$_{0.5}$/Si heterostructure, and in Fig. 7.5b the corresponding EDX maps. The maps show that Ge is present only in the initial SiGe part of the branches, while Si is present throughout the whole branch and more enriched in the final Si-only tip.

![Figure 7.5. Compositional characterization of junctions.](image)

(a) HAADF STEM image of a branch showing an initial hexagonal SiGe segment and a final pure Si part; (b) HAADF STEM image of a branch along with corresponding elemental EDX maps and a composite EDX map.
The flexibility of this method and the versatility of NWs is exemplified here. Indeed, in terms of lattice mismatch, it would make more sense to grow a Si-only branch part first and then transition to SiGe. This is logical due to the fact that the lattice constant of Si is much closer to that of GaP than Ge is and by mixing Ge in, we are essentially increasing the lattice constant. But by growing branch NWs on a suitable trunk sidewall, we achieve two things. First, by growing on the sidewall we are taking advantage of the trunk crystal structure in order to force the crystal to grow epitaxially in the desired hexagonal structure. Second, by depositing Au particles in order to grow (branch) NWs, we take advantage of the increased strain accommodation that NWs provide, which is due to their large aspect ratio.$^{143}$

In conclusion, we have fabricated defect-free $Si_{1-x}Ge_x$ NWs with the hexagonal diamond crystal structure by growing them epitaxially as branches on a suitable substrate trunk NW. In order to facilitate the VLS growth of the branch NWs, we deposited Au nanoparticles on the sidewalls of the trunks. It has been possible to fabricate $Si_{1-x}Ge_x$ NWs throughout the whole stoichiometric range and even more complex and abrupt SiGe heterostructures. This approach has thus allowed us to even further exploit the versatility of VLS NW growth to fabricate 3-dimensional heterostructures. We pave the way for the study of the optical properties of hexagonal diamond Si and SiGe, hopefully confirming the directness of the SiGe bandgap. This brings the possibility of realizing optical functionality to Si technology one step closer.
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(94) Rhodius Program
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Summary

Growth of Hexagonal Group-IV Semiconductor Nanowires

Band gap engineering in semiconductor materials can be achieved by a change in the periodic potential that affects the charge carriers. One way this can be practically achieved, is by changing the distance between the atoms of the lattice. This can be accomplished by growing the semiconductor crystal in another crystal structure. Implementation of this at the nanoscale, in this case with nanowires (NWs), is favored, because of the higher tolerances and elastic limits. Nanowires, with their one-dimensional (1D) geometry are thus an excellent candidate for our studies.

Bulk silicon (Si) and germanium (Ge) which possess the diamond cubic crystal structure, have notorious and well-established indirect band gaps, even though most semiconductors are direct gap materials. This indirect band gap makes Si and Ge rather inadequate in terms of their interaction with light. On the contrary, Si and Ge with the hexagonal crystal structure are predicted to exhibit a different band structure than their cubic counterparts. Ge with the hexagonal crystal structure is expected to possess a direct band gap while Si with the hexagonal crystal structure can be combined with hexagonal Ge to form a hexagonal SiGe alloy and further tune the direct band gap of hexagonal Ge to suit our demands. This contributes to make the crystal growth of hexagonal Si, Ge and SiGe alloy, a highly desirable goal.

In this thesis, we present the growth of Si and SiGe with a high quality hexagonal crystal structure and compositional tunability of the alloy, demonstrating for the first time the structural quality with a variety of experimental techniques and advanced methods.

The first goal was to learn to grow hexagonal Si crystals which is elaborated in Chapter 4. To this end, we utilized the crystal structure transfer technique and attempted to grow hexagonal Si as a shell around a hexagonal gallium phosphide (GaP) core NW. While on this path, we discovered the formation of a type of defects known as cracks, never before observed in nanowires, but also a number of others such as type-I1 stacking faults (SFs) and Frank partial dislocations. Their numerous appearance was not expected to this extent and an alternate pathway was proposed where a domino effect would take place creating more defects. At the growth temperature of 750 °C, only the cracks were observed, while at the growth temperature of 800 °C, the type-I1 SFs and Frank partials were observed. It was postulated that crack formation in core/shell nanowires could be understood to arise from a thermally induced strain gradient in the system. Furthermore, between 750 °C and 800 °C, the brittle-to-ductile transition (BDT) would take place in the Si shell, allowing type-I1 SF and Frank partial generation to take place from the initial cracks, in accordance to a domino effect.
The results of the previous discoveries allowed us to optimize the growth conditions and grow defect-free hexagonal Si at the high temperature of 900 °C, the results of which are presented in Chapter 5. In order to confirm the structural quality, we performed transmission electron microscopy (TEM) studies, viewing in several directions, both perpendicular and parallel to the growth direction. The results revealed an excellent hexagonal crystal phase purity of the Si shell, even for the largest volumes grown, such as NWs of a length up to 7.5 μm and shell thicknesses from 5–170 nm thick. The TEM studies further revealed the hexagonal Si lattice constants of $c_{\text{Si}} = 0.634$ nm and $a_{\text{Si}} = 0.389$ nm. X-ray diffraction (XRD) studies were also undertaken, allowing a large ensemble of NWs to be measured in order to get a more precise estimate of the lattice constants. It was found that by XRD $c_{\text{Si}} = 6.3237 \pm 0.0006$ Å and $a_{\text{Si}} = 3.8242 \pm 0.0006$ Å, thus refining the TEM results. Moreover, Raman spectroscopy studies were carried out where new Raman active modes were observed as compared to cubic Si to further strengthen our claim. We also performed high pressure Raman experiments with a diamond anvil cell as well and did not observe any structural phase transition all the way up to 9 GPa. Even after the release of the pressure back down to 0 GPa the Raman spectrum fully recovered its original characteristics.

Refining upon the foundation already laid down, we set out to grow hexagonal SiGe and the results are presented in Chapter 6. SiGe with a Ge content of about 65% could present a direct band gap around 1.7 μm, close to the telecommunication wavelength range. By growing at 600 °C, we were able to achieve excellent hexagonal crystal phase quality of smooth layer grown SiGe shells up to a Ge content of 77%, as evidenced by TEM studies performed perpendicular and parallel to the growth direction. As expected, we did observe the different growth modes of the shell with increasing Ge%, transitioning from layer-by-layer growth at the low Ge% end, to layer-plus-island and to only islands at the high end. We also performed growths at 700 °C and remarkably found that even though more Ge gets incorporated into the shell, the transition from layer-by-layer to layer-plus-island happens for lower Ge% (60%) than for the growths at 600 °C.

Finally, we aimed at directly growing hexagonal Si and SiGe NWs. This was achieved by inducing epitaxial vapor-liquid-solid (VLS) growth directly on hexagonal substrates, in this case being the sidewalls of hexagonal GaP NWs. The results are presented in Chapter 7. Having hexagonal nanowires in contrast to core/shell structures has the benefit that they can be isolated and various experiments can be performed avoiding any interfering signal and making the interpretation easier, while avoiding any potential unwanted doping from the core to the shell. TEM experiments revealed the excellent quality of the hexagonal Si and SiGe NWs, again in both perpendicular and parallel viewing directions. Furthermore, we were able to construct even more complex
heterostructures by growing NWs with Si and SiGe segments sequentially within the same NW, showcasing the excellent strain accommodation property of NWs.

The next step would be to perform measurements in order to determine whether or not the band gap of SiGe is direct and at what Ge content. The outlook of this work is grandiose and the potential payoff could be immense; an optically active Si-based component at the nanoscale that could be an integral part of future photonic circuits.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
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<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
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<td>GaP</td>
<td>Gallium Phosphide</td>
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<td>S</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
<tr>
<td>PIC</td>
<td>Photonic Integrated Circuit</td>
</tr>
<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
<tr>
<td>SiGe</td>
<td>Silicon-Germanium</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal-organic Vapor Phase Epitaxy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
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<td>ZnS</td>
<td>Zinc Sulfide</td>
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<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>LDA</td>
<td>Local-Density Approximation</td>
</tr>
<tr>
<td>LED</td>
<td>Light-Emitting Diode</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>F-M</td>
<td>Frank–van der Merwe (Layer-by-layer growth)</td>
</tr>
<tr>
<td>V-W</td>
<td>Volmer-Weber (Island growth)</td>
</tr>
<tr>
<td>S-K</td>
<td>Stranski–Krastanov (Layer-plus-island growth)</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
</tr>
<tr>
<td>Si₃H₆</td>
<td>Disliane</td>
</tr>
<tr>
<td>InAs</td>
<td>Indium Arsenide</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
</tr>
</tbody>
</table>
PDMS.................. Polydimethylsiloxane
PMMA.................. Polymethylmethacrylate
TMOS.................. Tetramethoxyorthosilicate
MTMS.................. Methyltrimethoxysilane
RIE...................... Reactive-Ion Etching
CHF₃...................... Fluoroform
[(CH₃)₂CO].......... Acetone
MO...................... Metalorganic
TMG(a).................. Tri-Methyl-Gallium
GeH₄..................... Germane
PH₃...................... Phosphine
CCS............... Close Coupled Showerhead
IR...................... Infrared
HCl...................... Hydrogen Chloride
SE..................... Secondary Electrons
BSE.................... Back-Scattered Electrons
STEM.................. Scanning TEM
DP...................... Diffraction Pattern
CCD.................. Charge-Coupled Device
BFP.................. Back Focal Plane
BFTEM.................. Bright-Field TEM
DFTEM.................. Dark-Field TEM
HRTEM.................. High-Resolution TEM
FFT.................. Fast Fourier Transform
ADF.................. Annular Dark Field
HAADF.................. High-Angle Annular Dark Field
EDX.................. Energy-Dispersive X-ray
FIB.................. Focused Ion Beam
Cₛ.................. Spherical aberration
C₇................. Chromatic aberration
RSM.................. Reciprocal Space Map
ESRF.............. European Synchrotron Radiation Facility
BDT.................. Brittle-to-Ductile Transition
JEMS .................. Java Electron Microscopy Image Simulation
VS .................. Vapor-Solid
FEM .................. Finite Element Modeling
FWHM ................. Full Width at Half Maximum
SF .................. Stacking Fault
TO .................. Transverse Optical
LO .................. Longitudinal Optical
FIB .................. Focused Ion Beam
Publications

Peer-Review Journal Publications


Conference Proceedings

Curriculum Vitae

Håkon Ikaros T. Hauge was born in 1982 in Athens, Greece.

He studied at the School of Applied Mathematical and Physical Sciences at the National Technical University of Athens, where he majored in Applied Physics with (i) Optoelectronics and Lasers and (ii) Advanced Technical Materials subfields. The diploma dissertation “Passivation of GaAs Surface Carriers by Al and Se” was carried out at the Epitaxy and Surface Science Laboratory of the National Center for Scientific Research “Demokritos”, Greece. He was awarded a MSc in Applied Physics in 2010.

Since June 2011, he has been employed as a PhD candidate at the Photonics and Semiconductor Nanophysics group under prof. dr. E.P.A.M. Bakkers at the Eindhoven University of Technology, The Netherlands, focusing on growth and study of nanowires.

In 2017, he was awarded the Marie Skłodowska-Curie Actions Seal of Excellence of the European Commission for his proposal NOVA: Novel Silicon and Germanium Allotropes.
Acknowledgement

One of the most important aspects of any scientific endeavor is collaboration. The idea that a collective intellect is much more capable of finding the answer to the archetypal question “why?”. As the driving force behind the formation of society, so in science collaborative effort shows that the “The whole is greater than the sum of its parts” – Aristotle. So, I would like to warmly acknowledge the people that directly or indirectly, more or less, contributed to this thesis and without whom, it would not have been possible.

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These last years at the TU/e in The Netherlands have been very interesting for me. I’ve been surrounded by people of extraordinary intellect and talent and whose plethora of different ways of approaching problem solving and science have been inspiring. To all of you, thank you for making my life experience richer.