

*Energy/Strain Analysis of GaAs and Axial/
Radial Core – Shell NWs with GaAs Core*

DISSERTATION

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Nanodrähte haben sich als äußerst vielseitige Plattform für die Entwicklung fortschrittlicher Heterostrukturen erwiesen, insbesondere dort, wo große Gitterfehlpassungen ein kohärentes Wachstum in planaren Konfigurationen verhindern. In dieser Arbeit werden die Dehnungs- und thermischen Eigenschaften von GaAs- und $\text{In}_x\text{Ga}_{1-x}\text{As}$ Kern-Mantel-Nanodrähten systematisch mithilfe theoretischer Modelle sowie experimenteller Methoden auf Synchrotronbasis untersucht.

Zunächst wird ein theoretischer Ansatz zur Modellierung der Dehnungsverteilung in gebogenen Nanodrähten entwickelt, der zeigt, wie mechanische Verformung die Bandstruktur und optoelektronischen Eigenschaften beeinflusst. Anschließend wird die Dehnungsrelaxation in GaAs/ $\text{In}_x\text{Ga}_{1-x}\text{As}$ -Nanodrähten experimentell mittels axialer und lateraler Röntgenbeugung untersucht. Für Indiumkonzentrationen über 50 % wird ein Übergang von elastischer zu plastischer Relaxation beobachtet, begleitet von der Bildung indiumreicher Oberflächenhügel, die zeitgleich mit kohärenten Schalen wachsen. Dies wird durch REM-Bilder und 3D-Dehnungskartierungen bestätigt.

Das transiente strukturelle Verhalten der Nanodrähte bei Bestrahlung mit Femtosekundenlaserpulsen wird mithilfe eines optischen Pump-Röntgen-Probe-Verfahrens untersucht. Die Ergebnisse zeigen, dass die thermische Ausdehnung proportional zur Laserleistung ist und stark von der Geometrie der Nanodrähte abhängt. Dabei zeigen die Zinkblende-

und Wurtzitphasen unterschiedliche thermische Reaktionen auf die Anregung.

Abschließend wird die axiale Verteilung von Beryllium-Dotierstoffen nahe der Nanodrahtoberfläche durch orts aufgelöste Röntgenphotoelektronenspektroskopie (XPS) analysiert. Die Verschiebung des Fermi-niveaus dient zur Bestimmung der lokalen Dotierstoffkonzentration und zeigt einen Gradienten entlang der Wachstumsachse, verursacht durch Abschattungseffekte während der Molekularstrahlepitaxie.

Diese Arbeit liefert ein umfassendes Verständnis der Dehnung, thermischen Dynamik und Dotierungsverteilung in Kern-Mantel-Nanodrähten und bietet wichtige Erkenntnisse für die gezielte Entwicklung nanoskaliger Halbleiterbauelemente.

Nanowires have emerged as a promising platform for the development of advanced hetero-structures, particularly where large lattice mismatches prevent coherent growth in planar configurations. In this thesis, strain and thermal behavior in GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ core-shell nanowires are systematically investigated using both theoretical modeling and synchrotron-based experimental techniques.

A theoretical approach is first established to model strain distributions in bent nanowires, revealing how mechanical deformation influences band structure and optoelectronic properties. Subsequently, strain relaxation in GaAs / $\text{In}_x\text{Ga}_{1-x}\text{As}$ nanowires is experimentally examined through in-plane and axial X-ray diffraction. A critical transition from elastic to plastic strain relaxation is observed for indium concentrations exceeding 50%, with the formation of indium-rich surface mounds coexisting with coherent shells, confirmed by SEM and 3D strain mapping.

The transient structural response of nanowires to femtosecond laser pulses is studied via an optical pump-X-ray probe setup. The results show that thermal expansion scales with laser power and is strongly dependent on nanowire geometry. Notably, zinc blende and Wurtzite phases exhibit distinct thermal behaviors under pulsed excitation.

Finally, the axial distribution of beryllium dopants near the nanowire surface is probed using spatially resolved X-ray photoelectron spectroscopy (XPS). The Fermi level shifts are used to map local dopant concentrations, revealing a gradient along the nanowire growth axis attributed to flux shadowing effects during molecular beam epitaxy.

Together, these findings provide a comprehensive understanding of strain, thermal dynamics, and dopant distribution in core-shell nanowires, offering insights critical for the design and optimization of nanoscale semiconductor devices.

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Introduction

*T*he continuous scaling of semiconductor devices has shifted the focus of modern research toward low-dimensional systems, where material properties can be tailored beyond the limitations of conventional bulk and planar structures. Among these systems, semiconductor nanowires have attracted significant attention due to their unique geometry, which enables the integration of materials with dissimilar lattice parameters while maintaining high crystalline quality.

In particular, III–V core–shell nanowires offer a versatile platform for engineering electronic and optical properties through controlled variation of composition, strain, and doping. However, the same structural flexibility that makes these systems attractive also introduces fundamental challenges. The interplay between lattice mismatch, mechanical relaxation, and defect formation remains insufficiently understood, especially under realistic growth conditions and device-relevant geometries.

One of the key open questions concerns the limits of strain accommodation in core–shell nanowires. While their free surfaces are often assumed to delay or suppress defect formation, experimental observations suggest that this assumption is only valid within a restricted parameter range. Beyond a certain threshold, strain relaxation mechanisms change in nature, leading to irreversible structural modifications. A detailed understanding of this transition is essential for establishing reliable design criteria for defect-controlled hetero-structures.

In addition to static strain effects, nanowires in practical applications are frequently exposed to non-equilibrium conditions, such as intense optical excitation. Under these conditions, rapid energy transfer to the lattice can induce transient structural changes on ultrafast timescales. The extent to which such processes remain reversible, and how they are influenced by pre-existing strain and crystal structure, is still not fully clarified.

Another important aspect is the incorporation and spatial distribution of dopants. In nanowire systems, dopant profiles are strongly affected by growth geometry and surface-related processes, often leading to non-uniform distributions along the growth direction. Since doping directly determines the electronic functionality of nanowire-based devices, a quantitative understanding of these inhomogeneities is crucial.

This dissertation addresses these challenges through a combined theoretical and experimental investigation of GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ core-shell nanowires. A theoretical framework is developed to describe strain in nanowires under mechanical deformation, providing insight into its influence on electronic properties. High-resolution X-ray diffraction experiments are then employed to analyze strain relaxation and identify the transition between different mechanical regimes. Furthermore, time-resolved optical pump-X-ray probe techniques are used to investigate the dynamic lattice response under ultrafast excitation. Finally, spatially resolved photoelectron spectroscopy is applied to determine dopant distributions and their relation to growth-induced effects.

By connecting structural, thermal, and electronic aspects, this work establishes a comprehensive picture of how different physical mechanisms interact in semiconductor nanowires. The results contribute to a deeper understanding of the limits and possibilities of strain engineering and provide guidance for the development of reliable nanoscale optoelectronic devices.

Theoretical Approach to Strain Components

Calculation of a Considered Bent Nanowire

2.1 Introduction

Nanowire electronic devices are subject of recent research as they can be used in a wide spectrum of applications such as displays, piezoelectric generators, energy storage devices and renewable energy.¹ The unique geometry and properties of semiconductor nanowires have stimulated their use for novel devices. To optimize their application, a detailed understanding of the nanowire material properties is of great importance. For example, it has been found that nanowire crystal structures are affected by and can be controlled with their growth parameters.² Beside that, most of the time, the modern nanoelectronics rely to a large degree on the properties of interfaces between two heterostructured semiconductors.³ In nanowires, strain primarily arises when two crystalline materials with different lattice parameters are combined to form a heterostructure. In addition, nanowires present other instances where strain may occur.⁴

In addition, even though the nanowire geometry allows for efficient strain relaxation via the surface, strain is in general known to alter the band structure in semiconductors, which has an impact in complex nanowire geometries. Externally applied forces will also affect the electronic properties of the nanowires, and information about the strain distribution within the wires becomes important for applications utilizing deformation of the nanowires.²

Strain engineering is actually widely used in advanced logic devices and has contributed to extend two-dimensional Si Complementary Metal–Oxide – Semiconductor (CMOS) technologies to at least the 32 nm node. Recent computational studies of the band structure of Si nanowires have

suggested that strain could also improve the performance of one dimensional nanowire device.⁵

However, in semiconductor nanowire investigation, strain in one side, is a efficient tool for calculating other involved quantities and on the other side is a great effective parameter for controlling some properties of nanowires. In this way, strain engineering is one of the very important strategies whose influence has been observed in all aspects of core-shell nanowires investigation. Therefore deeper understanding strain and strain engineering, can play great effective and great important role in research procedure in this field.

2.2 Definition of Stress

To keep a body in static equilibrium the sum of all forces acting on must be zero. If a small cubic volume as depicted in Figure 2.1 of the body is considered, and the forces ΔF_i act on the surfaces ΔA_i , the stress vector T_i is then defined as⁶ follow. The index i indicates one of the surface planes.

$$T_i = \lim_{\Delta A_i \rightarrow 0} \frac{\Delta F_i}{\Delta A_i} = \frac{dF_i}{dA_i} \quad (2.1)$$

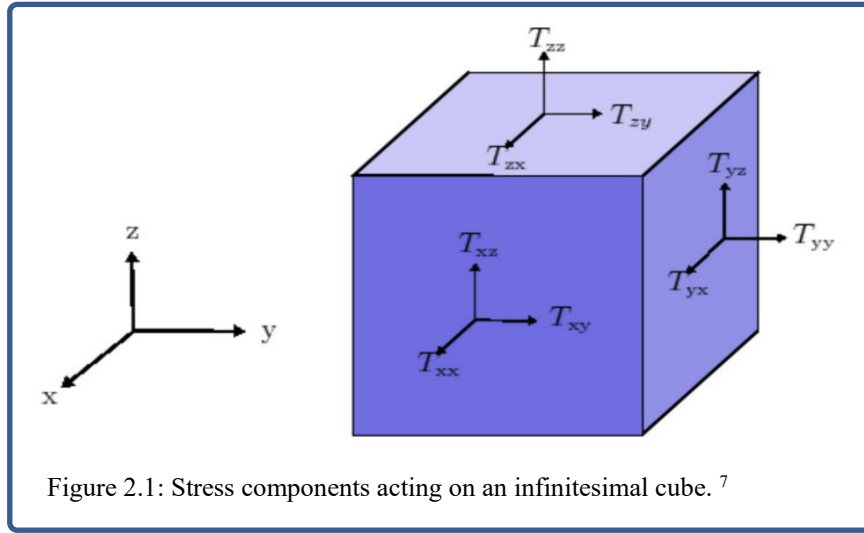
As depicted in Figure 2.1, each of the three stress vectors can be decomposed into two components within the plane, the so called shear stress components, and one normal component. The total number of six shear stress components and three normal stress components can be lumped together into the stress tensor $\underline{T}$.⁷

$$\underline{T} = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{xy} & T_{yy} & T_{yz} \\ T_{xz} & T_{yz} & T_{zz} \end{pmatrix} \quad (2.2)$$

To fulfill the condition of static equilibrium, the shear stress components across a diagonal are identical,

$$T_{xy} = T_{yx}, \quad T_{yz} = T_{zy}, \quad T_{xz} = T_{zx} \quad (2.3)$$

which leads to six independent components in the stress tensor.



2.3 Definition of Strain

Stress forces within a body cause an elastic deformation which is called strain. Two points at locations $\mathbf{x}$ and $\mathbf{x} + d\mathbf{x}$ within a relaxed body move under deformation caused by stress to the locations $\mathbf{x} + \mathbf{u}(\mathbf{x})$ and $\mathbf{x} + d\mathbf{x} + \mathbf{u}(\mathbf{x} + d\mathbf{x})$. The absolute squared distance between the deformed points can then be obtained as ⁶

$$\sum_i (dx_i + u_i(\mathbf{x} + d\mathbf{x}) - u_i(\mathbf{x}))^2 = \sum_i (dx_i + \sum_j \frac{\partial u_i}{\partial x_j} dx_j)^2 \quad (2.4)$$

Since $d\mathbf{x}$ is considered to be a small displacement, a Taylor expansion around $\mathbf{x}$ can be performed, which gives for the absolute squared distance

$$\sum_i (dx_i + \sum_j \frac{\partial u_i}{\partial x_j} dx_j)^2 = \sum_i dx_i^2 + 2 \sum_{ij} dx_i \frac{\partial u_i}{\partial x_j} dx_j + \sum_{ijk} \frac{\partial u_i}{\partial x_j} dx_j \frac{\partial u_i}{\partial x_k} dx_k \quad (2.5)$$

Since the first term in (2.5) is the squared distance between the points in the relaxed system the change in the squared distance caused by strain $D(dx)$ becomes ⁷

$$\begin{aligned} D(dx) &= \sum_{ij} dx_i \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) dx_j + \sum_{ijk} \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} dx_i dx_j \\ &= \sum_{ij} dx_i \left[\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \sum_k \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right] dx_j \\ &= 2 \sum_{ij} dx_i \varepsilon_{ij} dx_j \end{aligned} \quad (2.6)$$

Here, ε_{ij} are the components of the strain tensor which are defined as

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_k \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right) \quad (2.7)$$

If the strain is small enough such that $\frac{\partial u_k}{\partial x_i} \ll 1$ holds, the second order term in (2.7) can be neglected. This simplifies the resulting tensor components to ⁷

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (2.8)$$

The strain tensor is therefore symmetric

$$\underline{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{pmatrix} \quad (2.9)$$

In literature sometimes the so called engineering shear strain definition is used. The engineering shear strain γ_{ij} for $i \neq j$ is given by the relation ⁷

$$\gamma_{ij} = \varepsilon_{ij} + \varepsilon_{ji} = 2 \varepsilon_{ij} \quad (2.10)$$

2.4 Stress-Strain Relation

By observation of the behavior of spring systems, Robert Hooke first identified a mathematical relation between stress and strain. Hooke's Law denotes

$$F = k x \quad (2.11)$$

Here, k is the material-dependent spring constant, F is the applied force, and x is the resulting deformation of the spring. Later Cauchy generalized Hooke's law for application to three dimensional elastic

$$T_{ij} = C_{ijkl} \varepsilon_{kl} \quad (2.12)$$

where C_{ijkl} is the elastic stiffness tensor of order four. The tensor contains 81 components. Since there are only six independent components in the stress and strain tensors they can be written in a contracted notation as six

component vectors. In this formulation the elastic stiffness tensor simplifies to a 6×6 matrix.⁷

The number of independent components in the elastic stiffness tensor is further reduced by symmetry properties of the considered crystal.⁸ For cubic semiconductors such as Si, Ge or GaAs, the elastic stiffness tensor contains only three independent components, c_{11} , c_{12} and c_{44} , which lead to a stress-strain relation of the form

$$\begin{pmatrix} T_{xx} \\ T_{yy} \\ T_{zz} \\ T_{yz} \\ T_{xz} \\ T_{xy} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \cdot \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{xz} \\ 2\varepsilon_{xy} \end{pmatrix} \quad (2.13)$$

The factor 2 in the notation of the off-diagonal elements of the strain tensor stems from the fact, that in literature the values of the elastic stiffness constants are usually given for the engineering strain notation. The values for the elastic stiffness constants of Si and Ge are given in Table 2.1.

Table 2.1: Stiffness constants of Si and Ge. Units are GPa.⁷

	c_{11}	c_{12}	c_{44}
<i>Si</i>	166.0	64.0	79.6
<i>Ge</i>	126.0	44.0	67.7

In the case that the stresses are known, the values for the strains have to be determined by inversion of (2.12). With the introduction of the elastic compliance tensor S_{ijkl} , the inverted equation reads

$$\varepsilon_{ij} = S_{ijkl} T_{kl} \quad (2.14)$$

or in matrix form for the specific symmetry properties of the diamond lattice

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{xz} \\ 2\varepsilon_{xy} \end{pmatrix} = \begin{pmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ s_{12} & s_{11} & s_{12} & 0 & 0 & 0 \\ s_{12} & s_{12} & s_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{44} \end{pmatrix} \cdot \begin{pmatrix} T_{xx} \\ T_{yy} \\ T_{zz} \\ T_{yz} \\ T_{xz} \\ T_{xy} \end{pmatrix} \quad (2.15)$$

The elastic compliance constants s_{ij} are related to the elastic stiffness constants c_{ij} by ⁷

$$s_{11} = \frac{c_{11} + c_{12}}{c_{11}^2 + c_{11} c_{12} - 2 c_{12}^2} \quad (2.16)$$

$$s_{12} = \frac{-c_{12}}{c_{11}^2 + c_{11} c_{12} - 2 c_{12}^2} \quad (2.17)$$

$$s_{44} = \frac{1}{c_{44}} \quad (2.18)$$

2.5 Stress Applied Along Symmetry Directions

Uniaxial stress applied along symmetry directions of the cubic crystal is of technological importance since it is preferably used in actual devices. The stress and strain tensors in the principal coordinate system of the crystal are given in the following for uniaxial stress of magnitude S applied along $[100]$, $[110]$, $[111]$ and $[120]$ directions, respectively ⁷. Here, the strain tensors are calculated by inserting the corresponding stress tensors in equation (2.15).

$$\underline{T}_{[100]} = S \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \underline{\varepsilon}_{[100]} = S \begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{12} & 0 \\ 0 & 0 & s_{12} \end{pmatrix}$$

$$\underline{T}_{[110]} = \frac{S}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \underline{\varepsilon}_{[110]} = \frac{S}{2} \begin{pmatrix} s_{11} + s_{12} & s_{44}/2 & 0 \\ s_{44}/2 & s_{11} + s_{12} & 0 \\ 0 & 0 & s_{12} \end{pmatrix}$$

$$\underline{T}_{[111]} = \frac{S}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}, \quad \underline{\varepsilon}_{[111]} = \frac{S}{3} \begin{pmatrix} s_{11} + 2s_{12} & s_{44}/2 & s_{44}/2 \\ s_{44}/2 & s_{11} + 2s_{12} & s_{44}/2 \\ s_{44}/2 & s_{44}/2 & s_{11} + 2s_{12} \end{pmatrix}$$

$$\underline{T}_{[120]} = \frac{S}{5} \begin{pmatrix} 1 & 2 & 0 \\ 2 & 4 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \underline{\varepsilon}_{[120]} = \frac{S}{5} \begin{pmatrix} s_{11}+4s_{12} & s_{44} & 0 \\ s_{44} & s_{12}+4s_{11} & 0 \\ 0 & 0 & 5s_{12} \end{pmatrix} \quad (2.19)$$

Biaxial strain can be introduced in Si by epitaxially growing a Si layer on an SiGe substrate, which features a different lattice constant. The Si layer adjusts to the lattice constant of the SiGe substrate and becomes globally biaxially strained. If the interface is a (001)-plane the strain tensor reads ⁷

$$\underline{\varepsilon}_{(001)} = \varepsilon_{\parallel} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -\frac{2c_{12}}{c_{11}} \end{pmatrix}, \quad (2.20)$$

where $\varepsilon_{\parallel}$ could be the strain in the interface plane, related to the lattice mismatch via

$$\varepsilon_{\parallel} = \frac{a_l - a_0}{a_0}. \quad (2.21)$$

Here a_0 denotes the lattice constant of relaxed crystal, and a_l that of the substrate layer. Note that biaxial strain in the (001)-plane leads to the same form of the strain tensor as uniaxial stress in [001] direction; the $\varepsilon_{\parallel}$ could also represent the axial strain arising in a bent nanowire and can be related to the bending radius by applying a simple geometrical approach. For this purpose, we consider a tiny small element of a NW has been bent mechanically. The element is small enough that we can take it as part of a circle with inner radius r_1 , outer radius r_2 , mean radius R and radius of an arbitrary point inside element of radius r . Figure 2.2c show this quantities for a tiny fine element of an arbitrary nanowire.

Based on geometry, we have

$$R = (r_1 + r_2) / 2 \quad (2.22)$$

$$l_1 = r_1 \Delta\theta, \quad l_2 = r_2 \Delta\theta, \quad (2.23)$$

Considering same numbers of atoms “ n ” in different radius along element, for a_i distance between the atoms in radius r_i , one can write

$$a_1 = r_1 \Delta\theta / n, \quad a_2 = r_2 \Delta\theta / n. \quad (2.24)$$

For inner layers a_i is smaller than a_0 (atom distance in case of straight nanowire), while for outer layers a_i is bigger than a_0 . For middle layer in $r = R$, we have $a = a_0 = R \Delta\theta / n$; with $\Delta a_i = a_i - a$, therefore we will have

$$\Delta a_1 = \frac{\Delta\theta}{n} \left(r_1 - \frac{r_1 + r_2}{2} \right), \quad \Delta a_2 = \frac{\Delta\theta}{n} \left(r_2 - \frac{r_1 + r_2}{2} \right) \quad (2.25)$$

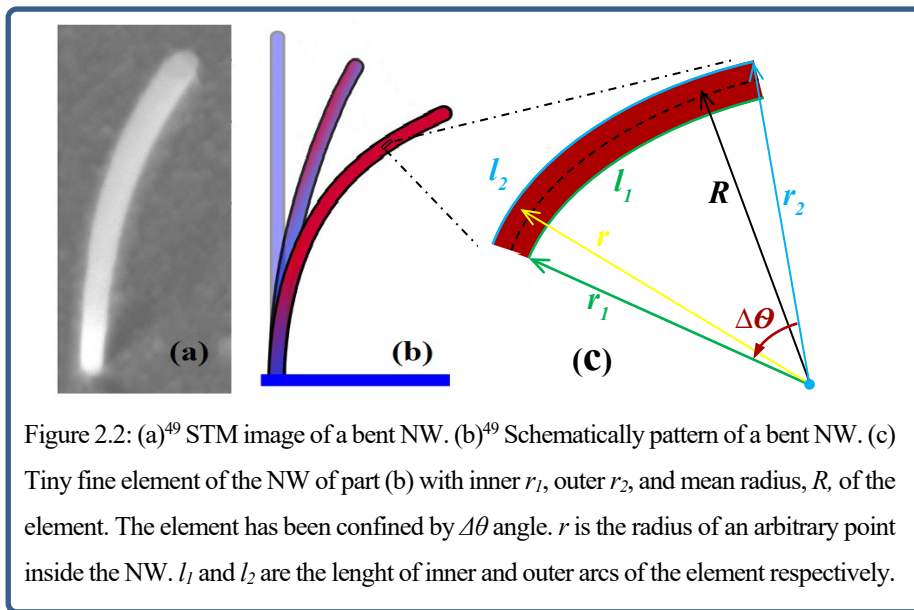
Using definition of strain, $\varepsilon_i = \Delta a_i / a$, and showing the strain along nanowire axis (axial component) by $\varepsilon_{\parallel}$, one can write

$$\varepsilon_{\parallel} = \frac{r}{R} - 1 \quad (2.26)$$

We define the coordinate system so that in every point, the z-axis be parallel to the axis of the nanowire on that point, then

$$\varepsilon_{\parallel} = \varepsilon_{zz} = \frac{r}{R} - 1 \quad (2.26)$$

Considering GaAs bent NW, and choosing coordinate system so z axis is in the $[111]$ direction, then the x and y axes are in the $[1\bar{1}0]$ and $[11\bar{2}]$ directions, respectively. Strain along $[111]$ direction $\varepsilon_{\parallel}$, will causes the strain in perpendicular directions with opposite sign. In this case it can be evaluated in hexagonal coordinate system by transforming the elastic



moduli from cubic crystal structure into hexagonal closed pack (*hcp*) structure using equations E.R. Fuller has used ⁹. The respective c_{ij} GaAs with *hcp* structure are

$$\frac{c_{12}}{c_{11}} = 0.285, \quad \frac{c_{13}}{c_{11}} = 0.224, \quad \frac{c_{33}}{c_{11}} = 0.230, \quad (2.27)$$

neglecting the small deformation of GaAs core lattice, the biaxial strain acting forms a pseudo square resulting in lattice expansion toward x-direction and y-direction are ¹⁰

$$\varepsilon_{xx} = -\frac{c_{12}}{c_{11}} \varepsilon_{yy} - \frac{c_{13}}{c_{11}} \varepsilon_{zz}, \quad \varepsilon_{yy} = -2 \frac{c_{12}}{c_{11}} \varepsilon_{zz} \quad (2.28)$$

$$\varepsilon_{zz} = \varepsilon_{\parallel} = \frac{a_{\parallel} - a_0}{a_0}, \quad \varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} = \frac{a_{\perp} - a_0}{a_0} = -2 \frac{c_{12}}{c_{11}} \varepsilon_{\parallel} \quad (2.29)$$

*Investigation of Strain Relaxation in GaAs/
In_xGa_{1-x}As Core-Shell Heterostructure NWs**

3.1 Introduction

One of the most beneficial qualities of core-shell NWs is the ability to sustain coherent shell growth beyond the critical thickness known from lattice mismatched planar systems. Additionally, surface passivation of the core by the surrounding shell can be utilized to enhance the efficiency of photo-emission because it reduces non-radiative surface recombination¹¹ and thereby enhances the opto-electronic properties of the device.

Above a critical lattice mismatch between the core and shell materials, the misfit strain can relax via the formation of misfit dislocations,¹² quantum dots¹³ and stress-driven surface roughening.¹⁴ These strain relaxation mechanisms within the NW core-shell system strongly depend on the diameter of the core, thickness of the shell and the lattice mismatch between the core and shell. For instance, Treu *et al.* have reported that a 10 nm thick InAs_{0.91}P_{0.09} shell grows coherently around an InAs core. However, an InP shell of the same thickness shows the formation of dislocations. Furthermore, it was revealed that the photoluminescence emission of this core-shell NW system intensify for higher P contents within the shell. This indeed indicates that the investigation of the strain relaxation mechanisms and critical composition of core-shell NWs are of paramount importance for the fabrication of high performance devices with NW hetero-structure.

*The results in this chapter are already published in Nanotechnology 2021, and I am co-author.

3.2 Sample Description

The samples investigated in this work are GaAs/ $\text{In}_x\text{Ga}_{1-x}\text{As}$ core-shell NW. Have been grown by Molecular Beam Epitaxy (MBE) on Si substrate. The core diameter is 140 nm and shell thickness is 18 nm. The nominal indium concentration inside the shell varies from 20% to 60% with steps of 10% for the five investigated samples (samples 1 to 5). Scanning electron microscopy (SEM) images of nanowires from samples 1-5 are displayed in Figure 3.1. The nanowires from samples 1-3 display a smooth surface whereas nanowires from samples 4-5 show rigidity defined by exterior presence of mounds. A detailed investigation of axial strain evolution of the mentioned samples has already been reported by R. B. Lewis¹⁵. Based on lab X-ray diffraction of the axial 111 Bragg reflection and transmission electron microscopy measurements, an anomalous strain relaxation process has been revealed for indium concentrations above 40%, where the surrounding $\text{In}_x\text{Ga}_{1-x}\text{As}$ grows simultaneously as a coherent shell and as plastically relaxed mounds at the edges along the nanowire growth axis (see Figure 3.1d,e). Driven by strain relief, mound growth is increasingly favored for increasing lattice mismatch. Moreover, it was unveiled that the mounds are indium rich compared to an indium poor shell. However, Ryan B. Lewis¹⁵ did not measure the radial lattice parameters preventing 3D strain analysis.

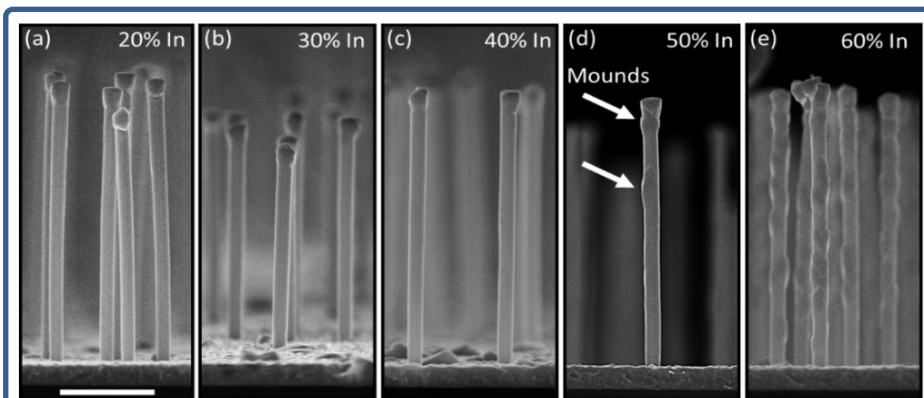


Figure 3.1: Panels (a) to (e) show SEM images of NWs from samples 1 to 5, respectively. The scale bar in (a) is 1 μm and applies to all SEM images.

In this work, we complement the above-described measurements by recording reciprocal space maps (RSMs) of the $2\bar{2}0$ and $22\bar{4}$ Bragg reflections, which are orthogonal to the nanowire growth axis, and normal to the side-facets and edges, respectively. From these diffraction maps, on the one hand, we confirm the appearance of plastic strain relaxation for indium concentrations above 40% resulting in the formation of indium rich mounds on top of an indium poor $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell, in agreement with Ryan B. Lewis¹⁵. On the other hand, we extend on these findings by calculating the 3D lattice deformation of the GaAs core and $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell at the edges and side-facets, revealing a strain variation of the core which reaches its maximum for nanowires with 50% of indium in the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell. Notably, for an indium concentration of 20%, the crystal lattice of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell at the side-facets and edges undergoes 3D compression.

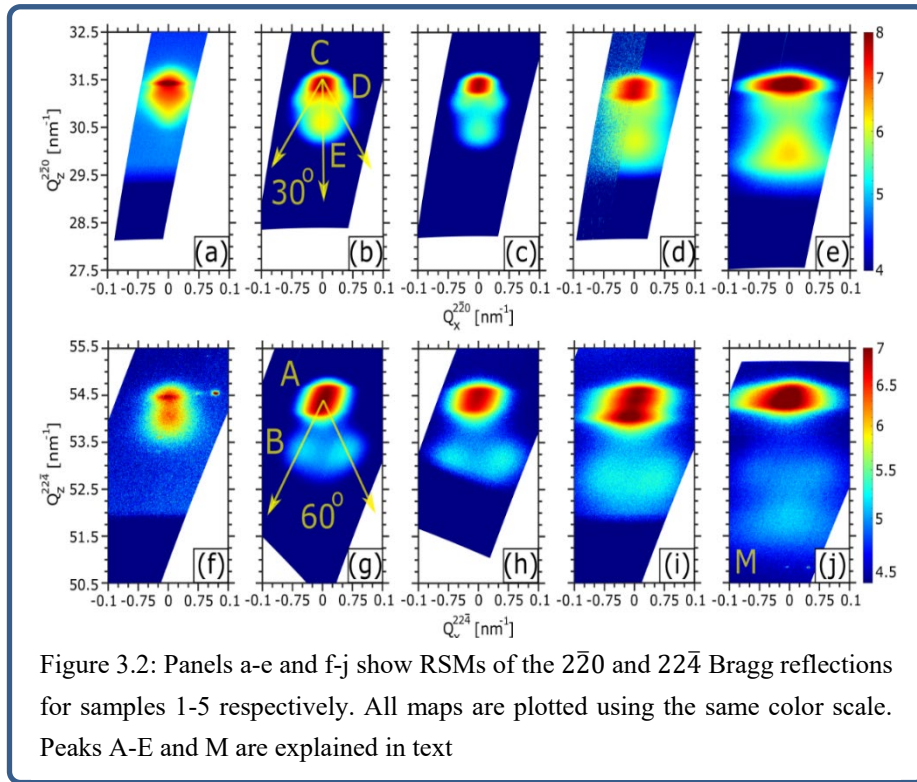
3.3 *Experiment and Results*

The X-ray diffraction measurements were carried out on as-grown nanowire ensembles at beamline 9 at the DELTA synchrotron in Dortmund with photon energy of 13 keV. To access the radial strain normal to the side facets and edges of the core and shell, rocking scans were performed in the vicinities of the $2\bar{2}0$ and $22\bar{4}$ in-plane Bragg reflections collecting the scattered intensity distribution using a two dimensional 100 k Pilatus detector placed 1 meter away from the sample. The experiment was executed in grazing incidence geometry where the angle of the incident beam with respect to the substrate surface was set to zero and the diffracted intensities of the $2\bar{2}0$ and $22\bar{4}$ Bragg reflections were measured in the plane perpendicular to the surface normal at Bragg angles at around 27.6° and 48.80° , respectively. The 2D intensity frames collected at each rocking angle were integrated to compose 2D RSMs of the respective Bragg reflections. More information about the diffraction setup, and equations used to translate from real space angular coordinates into reciprocal space vectors can be found by Ali Al-Hassan¹⁶.

RSMs of $22\bar{4}$ and $2\bar{2}0$ reflections are displayed in panels (a-e) and (f-j) of Figure 3.2, respectively, ranging from sample 1 to sample 5 (from left

to right). Reciprocal space vectors $Q_z^{2\bar{2}0}$ and $Q_z^{2\bar{2}\bar{4}}$ are defined along the scattering direction of the measured planes in reciprocal space. In other words, $Q_z^{2\bar{2}0}$ and $Q_z^{2\bar{2}\bar{4}}$ are sensitive to the variation in lattice spacing of the respective lattice planes.

The scattering peaks, named A-E, in the RSMs of Figures 3.2b and 3.2g can be explained by the strain impact on the lattice planes of different sections of the core-shell nanowire system.^{16, 17, 18} For better clarity, a schematic correlation between the respective RSMs recorded for sample 2, and animations of the core-shell nanowire cross-section overlapped by the $2\bar{2}\bar{4}$ and $2\bar{2}0$ lattice planes are illustrated in Figures 3.3a and 3.3b. We attribute peak C in the $2\bar{2}0$ RSMs to Bragg diffraction from the $2\bar{2}0$ lattice planes of the GaAs core. Sub-peaks D, making an angle of about 60° with $[2\bar{2}0]$, are explained by diffraction from the $[2\bar{2}0]$ lattice planes of neighboring $\text{In}_x\text{Ga}_{1-x}\text{As}$ side facets. Peak E, indicated by a red circle in Figure 3.3a, belongs to the $2\bar{2}0$ lattice planes of the measured couple of $\text{In}_x\text{Ga}_{1-x}\text{As}$ opposite side facets that are aligned horizontally with the GaAs



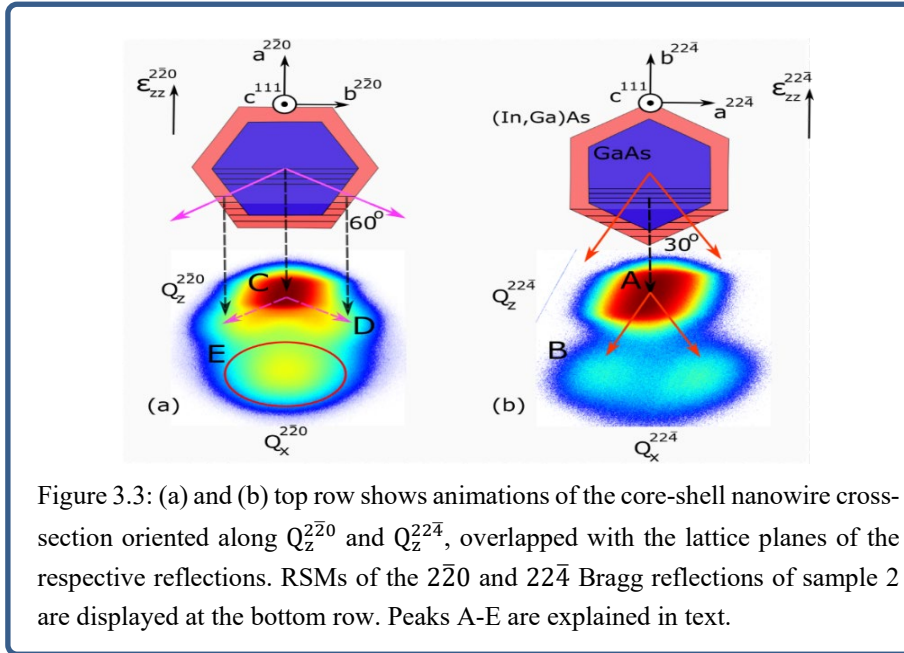
core. Peak A in the $22\bar{4}$ RSMs originates from the $22\bar{4}$ lattice planes of the GaAs core and the $\text{In}_x\text{Ga}_{1-x}\text{As}$ side facets that are aligned vertically onto the side walls of the core in Figure 3.3a. The two sub-peaks B, indicated by red arrows at lower $Q_z^{22\bar{4}}$ values, make an angle of 30° with $22\bar{4}$ and therefore originate from the $22\bar{4}$ lattice planes of the neighboring $\text{In}_x\text{Ga}_{1-x}\text{As}$ side facets. Interestingly for sample 5, an additional sub-peak, labelled by M, is visible at low $Q_z^{22\bar{4}}$ values (see Figure 3.2j), presumably originating from the $\text{In}_x\text{Ga}_{1-x}\text{As}$ mounds formed on top of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell (see Figure 3.1d,e). The same is expected for sample 4, as explained later, but it is not visible due to the too short scanning range (Figure 3.2i).

Qualitatively, the central peaks appearing at $Q_z^{22\bar{4}} = 54.5 \text{ nm}^{-1}$ and $Q_z^{2\bar{2}0} = 31.5 \text{ nm}^{-1}$ broaden along Q_z for increasing the nominal indium concentration in the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell. This reflects the higher strain variation that the core undergoes as the core-shell lattice mismatch increases. The broadest peak is observed for nanowires with 50% of nominal indium content. This is the transition point from elastic deformation to plastic strain relaxation via the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ aggregates found by R. B. Lewis¹⁵.

To estimate the strain variation in the core, the radial $2\bar{2}0$ and $22\bar{4}$ lattice constants and indium content of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell, we integrate the $2\bar{2}0$ and $22\bar{4}$ Bragg reflections along Q_x and fit the resulting line profiles, displayed in Figure 3.4, along Q_z by multi-Gaussians.

The red dashed lines at $Q_z^{22\bar{4}} = 54.5 \text{ nm}^{-1}$ and $Q_z^{2\bar{2}0} = 31.5 \text{ nm}^{-1}$ in Figure 3.4 indicate the positions of the respective unstrained lattice planes for GaAs. The cut vertical black lines represent the positions of unstrained $22\bar{4}$ and $2\bar{2}0$ $\text{In}_x\text{Ga}_{1-x}\text{As}$ lattice planes for the nominal indium concentration of the sample. The red peaks represent peaks B and E in $2\bar{2}0$ and $22\bar{4}$ respectively. The most intense peaks in $2\bar{2}0$ and $22\bar{4}$ are peaks A and C. Their broadening originates from the strain variation acting on the respective lattice planes of the GaAs core for peak C, and from the $2\bar{2}0$ lattice planes of the core and the $\text{In}_x\text{Ga}_{1-x}\text{As}$ facets which are aligned

vertically on the sides of the core (see Figure 3.3) for peak A. Representing the lower and upper edges of this variation by the green and blue Gaussians, the strain variation can be calculated from the difference between these two peaks. The values of strain variation calculated accordingly for the GaAs core for samples 1-5 are listed in Table 1. The pink Gaussian peak along $[2\bar{2}0]$ represents sub-peaks D. Conventionally, the Bragg peak of the substrate, supposed to be unstrained, is used as a reference to calculate the absolute strain in the nanowires. However, due to the absence of the Si peak in the diffraction pattern, we set the right edge of the core peak (colored in green in Figure 3.4) to the position of unstrained GaAs for both $2\bar{2}0$ and $2\bar{2}\bar{4}$. All other peaks have been shifted subsequently. This is an approximation because the GaAs core is affected by a small tensile strain induced by the surrounding shell which results in a tiny shift towards lower Q_z values. However, this effect is neglected. The $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell of the nanowires in sample 1 is compressed as the red peak is centered at a higher $Q_z^{2\bar{2}\bar{4}}$ value compared to the unstrained position which is indicated by a vertical cut line. For samples 2 (30% In) and 3 (40% In), the red Gaussian is almost centered at the $Q_z^{2\bar{2}\bar{4}}$ values of unstrained $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$ and $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ which leads into two possible



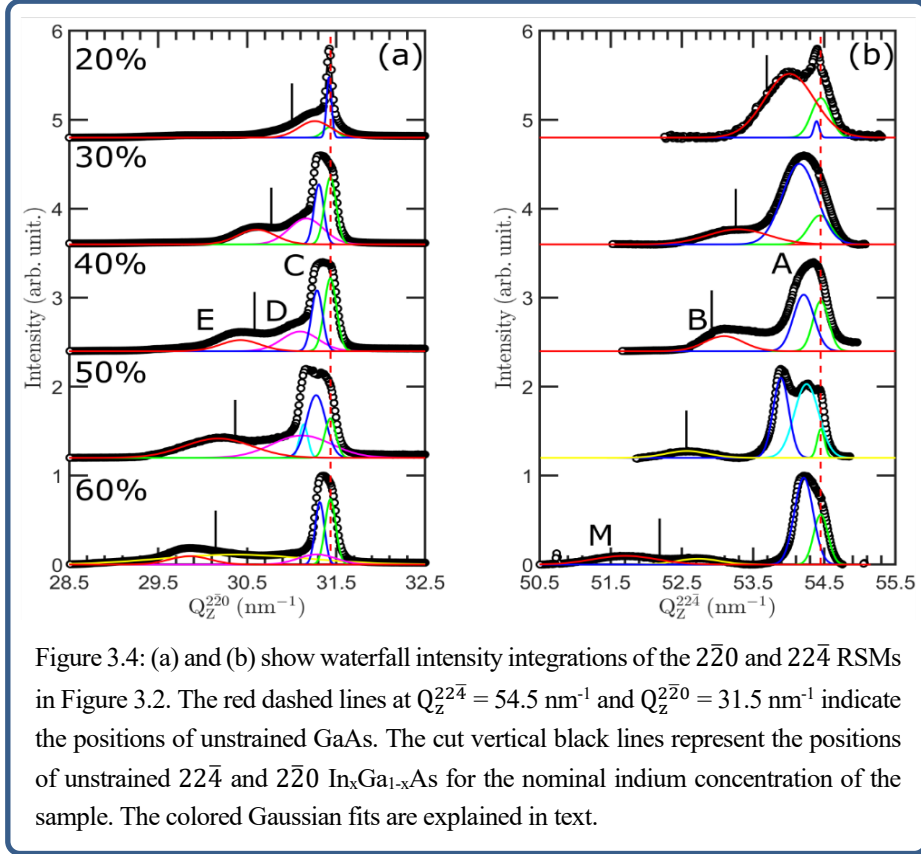
explanations. The first is that the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell is fully relaxed whereas the second is that the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell is strained, but the tetragonal distortion is at an angle, so the compression and expansion mostly cancel out resulting in an average peak that is found at the unstrained $Q_z^{2\bar{2}0}$. However, the $2\bar{2}0$ Bragg reflection of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell being visible at lower $Q_z^{2\bar{2}0}$ with respect to the unstrained value (peak E) indicates that the $\text{In}_x\text{Ga}_{1-x}\text{As}$ lattice is indeed strained and therefore negates the first explanation. For sample 5 (60% of indium), two peaks colored in red and yellow are visible along $2\bar{2}0$ and $22\bar{4}$. The red peaks are at lower $Q_z^{2\bar{2}0}$ and $Q_z^{22\bar{4}}$ values compared to the unstrained position whereas the yellow Gaussians are at higher ones. This indicates that the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell is indeed formed of two volumes with different indium concentrations higher and lower than 60%, which shall be discussed later. As the nanowires of samples 4 and 5 show the formation of mounds at the nanowire surface, $\text{In}_x\text{Ga}_{1-x}\text{As}$ of sample 4 is expected to be represented by two Bragg peaks, similar to sample 5. However, the second peak presumed to originate from the mounds is outside the scanning range and therefore is not visible in Figure 3.4.

The peak positions extracted from the Gaussian fits were translated into strain values using the equation below

$$\varepsilon_{hkl}^{(\text{In,Ga})\text{As}}(\%) = \frac{Q_z^{(\text{In,Ga})\text{As}} - Q_{\text{unstrained}}^{\text{GaAs}}}{Q_{\text{unstrained}}^{\text{GaAs}}} \times 100 \quad (3.1)$$

The strain values extracted from the Gaussians are listed in Table 3.1 and are plotted in Figure 3.5. The colors of the data points are correlated with those of the Gaussian fits in Figure 3.4. The horizontal black lines represent the theoretical lattice mismatch between GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a function of the nominal indium content. Looking at the separation between the blue and green data points, the strain variation in the core reaches a maximum of $0.94 \pm 0.22\%$ and $1.03 \pm 0.29\%$ along $2\bar{2}0$ and $22\bar{4}$ for the sample with 50% of indium content before relaxing down to $0.36 \pm 0.24\%$ and $0.44 \pm 0.34\%$ for the sample with 60% of indium. The values of the strain variation for samples 1-5 are listed in Table 3.1. The same

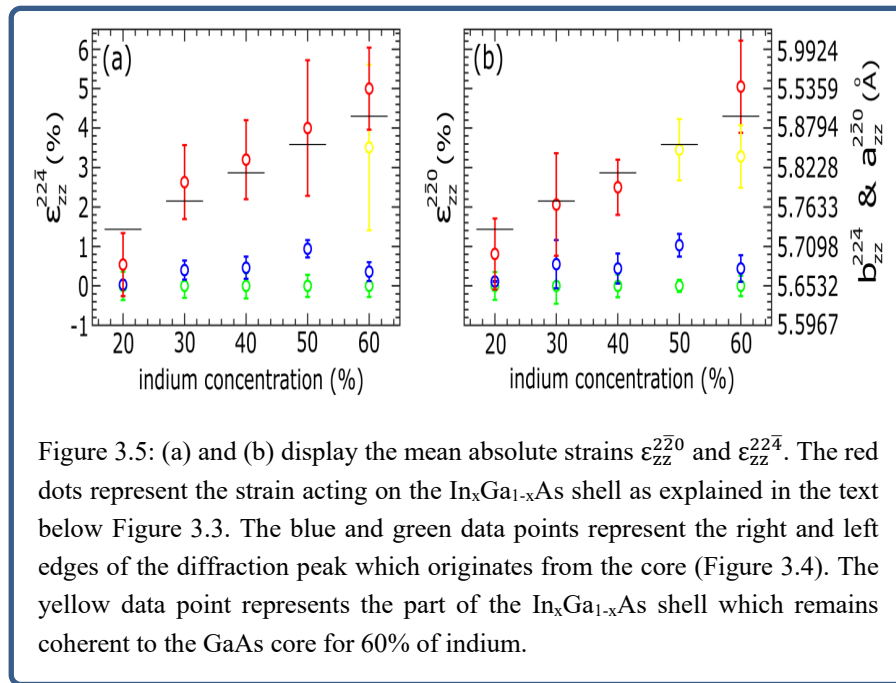
behavior was observed axially for the GaAs core and the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell by R. B. Lewis¹⁵. However, it was reported that the strain release starts from the sample with 50% of indium within the shell. The red data points being centered beyond the unstrained position along $2\bar{2}0$ reveal that the $2\bar{2}0$ lattice planes of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell undergo higher expansion compared to the $2\bar{2}\bar{4}$ lattice planes resulting from the compression along 111. A similar higher lattice expansion along $2\bar{2}0$ has been observed by Leila Balaghi¹⁹ for the GaAs cores when surrounded by thicker $\text{In}_x\text{Ga}_{1-x}\text{As}$ shells. Interestingly, the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell of the nanowires of sample 1 is compressed in all directions. The yellow and red data points at higher and lower $\varepsilon_z^{2\bar{2}\bar{4}}$ and $\varepsilon_z^{2\bar{2}0}$ values compared to the theoretical lattice mismatch between GaAs and $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}$ (see Figures 3.5 and 3.6) are both associated with $\text{In}_x\text{Ga}_{1-x}\text{As}$ in nanowires of sample 5. The first originates from an $\text{In}_x\text{Ga}_{1-x}\text{As}$ volume with an indium concentration higher than 60% whereas the second shows a lower indium content. The TEM



data from R. B. Lewis¹⁵ suggests that the mounds are indium rich whereas the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell underneath is indium poor. The error bars were calculated taking into consideration the FWHM of the Gaussians as an input for equation 3.1.

Table 3.1: Strain values along $[2\bar{2}0]$ and $[22\bar{4}]$ for the GaAs core and the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell and mounds extracted from the colored Gaussian in Figure 3.4, and plotted in Figure 3.5. The strain values along $[111]$ are taken from Ref. No. 15. “m” is mounds and “s” is shell

In	$\varepsilon_{zz}^{2\bar{2}0}$ (%)		$\varepsilon_{zz}^{22\bar{4}}$ (%)		ε_{zz}^{111} (%)
	Blue- Green	Red	Blue- Green	Red	
20%	0.03 ± 0.12	0.54 ± 0.80	0.11 ± 0.10	0.81 ± 0.90	0.45
30%	0.40 ± 0.24	2.63 ± 0.94	0.55 ± 0.61	2.06 ± 1.3	0.70
40%	0.46 ± 0.28	3.20 ± 1.00	0.44 ± 0.38	2.50 ± 0.70	0.96
50%	0.94 ± 0.22	4.00 ± 1.72	1.03 ± 0.29	3.45 ± 0.78 (s)	0.74
60%	0.36 ± 0.24	5.00 ± 1.04 (m) 3.51 ± 2.10 (s)	0.44 ± 0.34	5.05 ± 1.17 (m) 3.28 ± 0.79 (s)	0.46

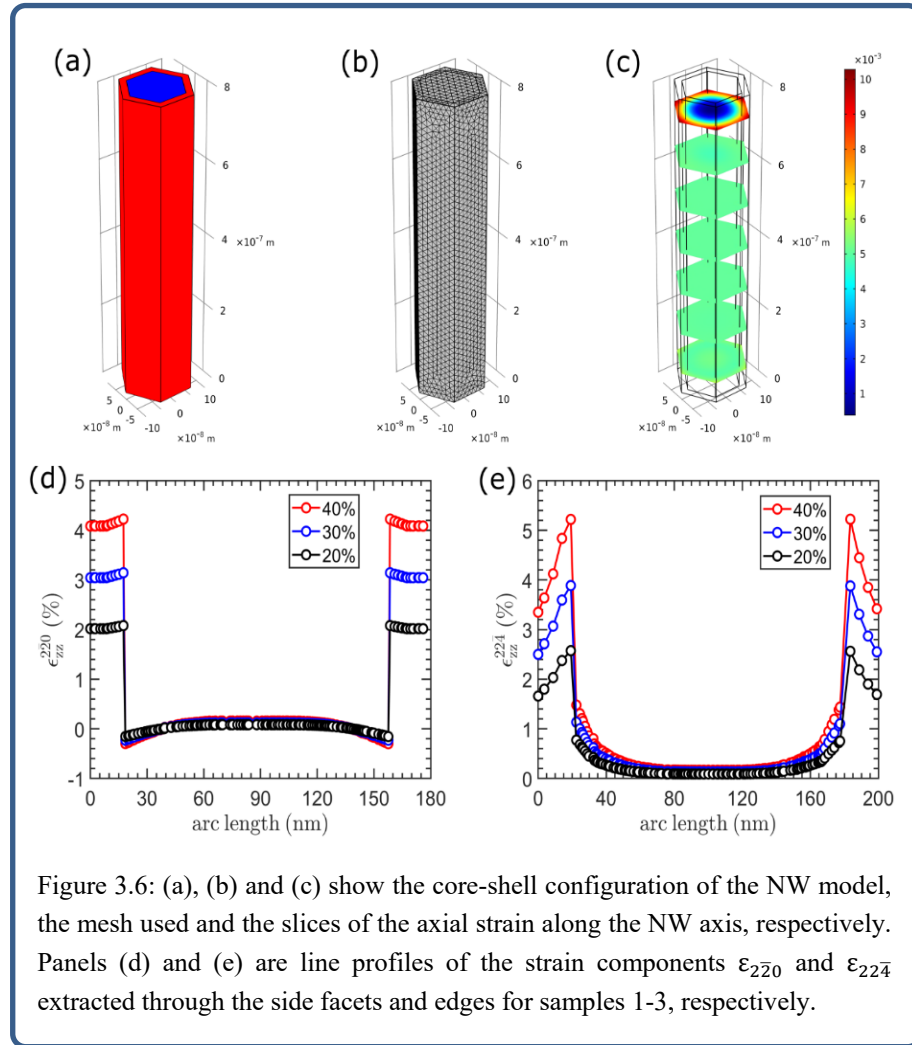


To get a better understanding of the 3D strain behavior in the core and shell, we performed an FEM simulation using a single nanowire model composed by a 140 nm thick GaAs core (blue colored volume in Figure 3.6a) and 18 nm $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell with indium concentration of 30% (colored in red). More details about the numerical input, meshing procedure (Figure 3.6b) and calculation scheme can be found in the FEM section of Ali Al-Hassan ¹⁶. Iso-surface slices of the axial strain are demonstrated in Figure 6c where apart from the upper section of the nanowire model, the core and shell share the same lattice parameter. Line profiles of the strain components $\varepsilon_{2\bar{2}0}$ and $\varepsilon_{22\bar{4}}$ (see Figure 3.3) extracted through one pair of opposite side facets and edges are displayed in the panels (d) and (e) of Figure 3.6, respectively. In confirmation to our assumption, the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell shows lattice expansion larger than the expected nominal lattice mismatch, as a result of the compression along the $[111]$ direction. Interestingly, the inner section of the GaAs core shows slight expansion along $[111]$, $[2\bar{2}0]$ and $[22\bar{4}]$, faced by compression as one approaches the core-shell interface. For instance, for the nanowire model with 30% nominal indium concentration, the inner volume of the GaAs core undergoes a lattice expansion of 0.15% along $[2\bar{2}0]$ and a maximum lattice compression of -0.20% at the core-shell interface, forming a strain variation of 0.35%. This is in agreement with the strain variation deduced experimentally from the difference between the green and blue Gaussian peaks of 0.41%. This experimental value might be overestimated because of normalization of the GaAs peak (see above).

3.4 Discussion

The investigation of the strain behavior in nanowire hetero-structures is essential for tuning the opto-electronic performance of the device. For instance, the strain induced by growing an $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell onto one side of a mismatched GaAs core has been utilized to control the bending radius of the nanowire ¹⁵. In addition, GaAs nanowire cores exhibit reduction of their bandgap by up to 40% when overgrown with lattice-mismatched thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ shells. ²

Nevertheless, For high lattice mismatches (indium content $> 40\%$), a thin $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell surrounding a thick GaAs core splits simultaneously into an indium poor coherent shell and indium rich $\text{In}_x\text{Ga}_{1-x}\text{As}$ mounds on top.¹⁵ In the present work, we confirm this phenomenon by the presence of two $\text{In}_x\text{Ga}_{1-x}\text{As}$ diffraction peaks along $[2\bar{2}0]$ and $[22\bar{4}]$ for sample 5 (yellow peak for the coherent shell and red peak for the mounds in Figures 4 and 5). The same is expected for sample 4, however the peak at lower $Q_z^{22\bar{4}}$ is out of scanning range. The lattice spacing of the mounds calculates to $5.9537 \text{ \AA}$ corresponding to a mismatch of $\approx 5.3 \%$ which is above the theoretical lattice mismatch considering 60% of indium by 1%. This reflects that the mounds are indeed indium rich compared to the underlying



$\text{In}_x\text{Ga}_{1-x}\text{As}$ shell. The average indium concentration extracted from the red diffraction peaks in $2\bar{2}0$ and $22\bar{4}$ using Vegard's law is around 75%, which is reported to reach up to 80% by R. B. Lewis¹⁵. The indium enrichment of the mounds coincides with an indium depletion of the neighboring shell regions. The yellow Bragg peaks representing the coherent $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell translates into a mean indium concentration of 45%. The yellow peak for sample 4 is closer to the theoretical lattice mismatch position which can be explained by the lower indium enrichment of the mounds for smaller lattice mismatch. However, the homogeneity of the indium distribution within the mounds depends on how indium diffuses from the shell into the mounds.

Furthermore, reflected by the broadening of its Bragg reflection along the scattering directions, $Q_z^{22\bar{4}}$ and $Q_z^{2\bar{2}0}$, the GaAs core undergoes a strain inhomogeneity, induced by the surrounding $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell. As the indium content within the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell increases from 20% to 50% (increasing lattice mismatch with constant core and shell dimensions), the strain variation acting on the core increases from $(0.03 \pm 0.12\%)$ to $(0.94 \pm 0.22\%)$ along $[2\bar{2}0]$ and from $(0.11 \pm 0.10\%)$ to $(1.03 \pm 0.29\%)$ along $[22\bar{4}]$. Interestingly, as the nominal indium content increases to 60% (Sample 4), the GaAs core relaxes as the strain variation drops down to $(0.36 \pm 0.24\%)$ along $[2\bar{2}0]$ and to $(0.44 \pm 0.34\%)$ along $[22\bar{4}]$. This has been observed axially by R. B. Lewis¹⁵, and can be explained by the favored growth of the mounds rather than a coherent shell for an increasing core-shell lattice mismatch. The thinner the shell is, the less is the amount of strain induced on the core.

The $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell at the side-facet acts as a thin layer deposited on top of a GaAs substrate, which compresses along $[111]$ and $[22\bar{4}]$ (c^{111} and $b_{(\text{In,Ga})\text{As}}^{2\bar{2}0}$) to match the in-plane lattice spacing of the GaAs core (c^{111} and $b_{\text{GaAs}}^{2\bar{2}0}$). This biaxial compression translates into expansion of $\text{In}_x\text{Ga}_{1-x}\text{As}$ beyond the theoretical unstrained lattice parameter along $[2\bar{2}0]$ ($a_{(\text{In,Ga})\text{As}}^{2\bar{2}0}$). This, indeed, has been experimentally validated and

illustrated in Figure 5 (red data points). However, in a very interesting phenomenon, the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell shows hydrostatic or tri-axial lattice compression for a nominal indium concentration of 20% (sample 2), which is not understood. The complete opposite is expected for the GaAs core, which is supposed to undergo only slight expansion, due to its much larger volume, which increases when approaching the hetero-interface. Moreover, supported by the FEM simulations in Figure 3.6, the GaAs core is expected to expand in all directions, being pulled apart by the surrounding lattice mismatched shell. Indeed, the GaAs core is simultaneously expanded axially and radially near the hetero-interface at the side-facets (blue data points in Figure 5). Similar behavior has been reported before for thin GaAs cores surrounded by a relatively thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell.¹⁹

*Thermal Expansion Investigating of GaAs and
GaAs/Al_xGa_{1-x}As NWs induced by fs-laser pulses*

4.1 Introduction

In the last century, a large diversity of research lines emerged targeting the fundamental and applied properties of the collective vibrations of lattice atoms of materials called phonons.²⁰ The continuous reduction of semiconductors dimensions in the past decades has opened possibilities to manipulate phononic and photonic properties at the micro- and nanoscale. With decreasing structure sizes, heat in the form of atomic vibrations can drastically modify material properties and limit the performance of devices. This fact poses a major challenge for the design of nanoscale devices due to the complexity of controlling the heat flow at the nanoscale.²⁰

The effect of femtosecond, ultrafast pulse heating of semiconductors has been associated with several fundamental dynamical processes that occur on the picosecond to nanosecond time scales like excitation and thermal equilibration of phonons.

In this part we have studied the transient structural response in *GaAs* NWs and *In_xGa_{1-x}As/GaAs* straight core shell NWs when irradiated with femtosecond laser pulses. An optical laser pump pulse will thermally excite the NWs that are probed with an X-ray pulse delayed by a certain time with respect to the pump pulse. *GaAs* is a direct band-gap semiconductor with a bandgap of 1.42 eV at room temperature. As the bandgap in semiconductors is a function of the lattice temperature, the transient changes of the lattice temperature can reflect the inter-band transition rate. Laser heating in semiconductors leads to electron ejection from an atomic core level and excitation of photoelectrons from the

valence to the conduction band. These hot electrons thermalize by electron–phonon and electron–Plasmon scattering and settle into the lowest states of the conduction band while interacting with lattice phonons, a process yielding the thermalization of conduction band. While electron–phonon scattering is much faster (~ 1 ps), the equilibration of optical and acoustic phonon temperature requires longer time.²¹ Before thermalization, the lattice temperature increases and the band gap decreases. This suggests that the thermal conductivity is time-dependent. Furthermore, axial linear thermal expansion coefficient of an infinite long NW would be affected by both the surface and axial crystal orientation. Different temperature dependencies of lattice parameter and thermal expansion coefficient were found for NWs with different width.²²

The fabrication process usually involves thermal cycles especially in the preparation of multilayer microelectronic devices, and the mismatch in the material thermal expansion coefficient will cause significant internal stress which induces the unacceptable degree of curvature or detachment during the production. It is well known that the behaviors of nanomaterials, e.g. nanowires, would be different from their bulk counterparts. Therefore, it is essential to have in-depth understanding regarding how the thermal expansion properties of semiconductor nanowires change with their sizes in order to improve the manufacturing quality.²²

The mechanical, optical, electric, and magnetic properties of nanowires, have been researched intensively²². These observations have indicated that, owing to the significant surface-to-volume ratio in nanomaterials, their thermal expansion coefficients may depend not only on temperature but also on geometric dimensions. Despite this, to the best of our knowledge, limited research has focused specifically on the thermal expansion behavior of nanowires. In the present study, we employ an optical pump–X-ray probe technique, utilizing a femtosecond laser beam for excitation and out-of-plane X-ray diffraction for time-resolved probing. This approach enables a detailed investigation of the thermal expansion dynamics in nanowires.

4.2 Experiment and Results

4.2.1 Samples Description

Two of the samples measured in this study are straight GaAs NWs and the third sample is a core/shell NWs with GaAs core and a strained InGaAs shell. All were grown by molecular beam epitaxy onto Silicon (111) substrate covered by native oxide²³. All samples are straight NWs sample with different total thickness named as samples No.1 sample No.2 and No.3. Sample No.3, is GaAs/(In,Ga)As core/shell NW with 30 nm thickness of shell including 10% In, and 100 nm core diameter (total diameter of NWs is 160 nm) and 2.89 μm length. All samples were grown in a microarray on a pre-patterned 111 oriented silicon substrate. Sample data are listed in table 4.1.

4.2.2 Measurement Description

Two series of samples in KMC-3 XPP (Single bunch) beam line in Helmholtz Zentrum in Berlin, have been measured in two different experimental campaigns. The out-of-plane thermal expansion in selectively grown arrays (micro fields) of GaAs NWs on silicon (111) substrate as well as time resolved response of NWs to the optical excitation done by laser pump with wave length of 514 nm and pulse width of 250 fs, has been performed by optical pump and X-ray probe setup available at KMC-3 XPP beamline. The ratio of core-shell composition and diameter were varied during the MBE growth.

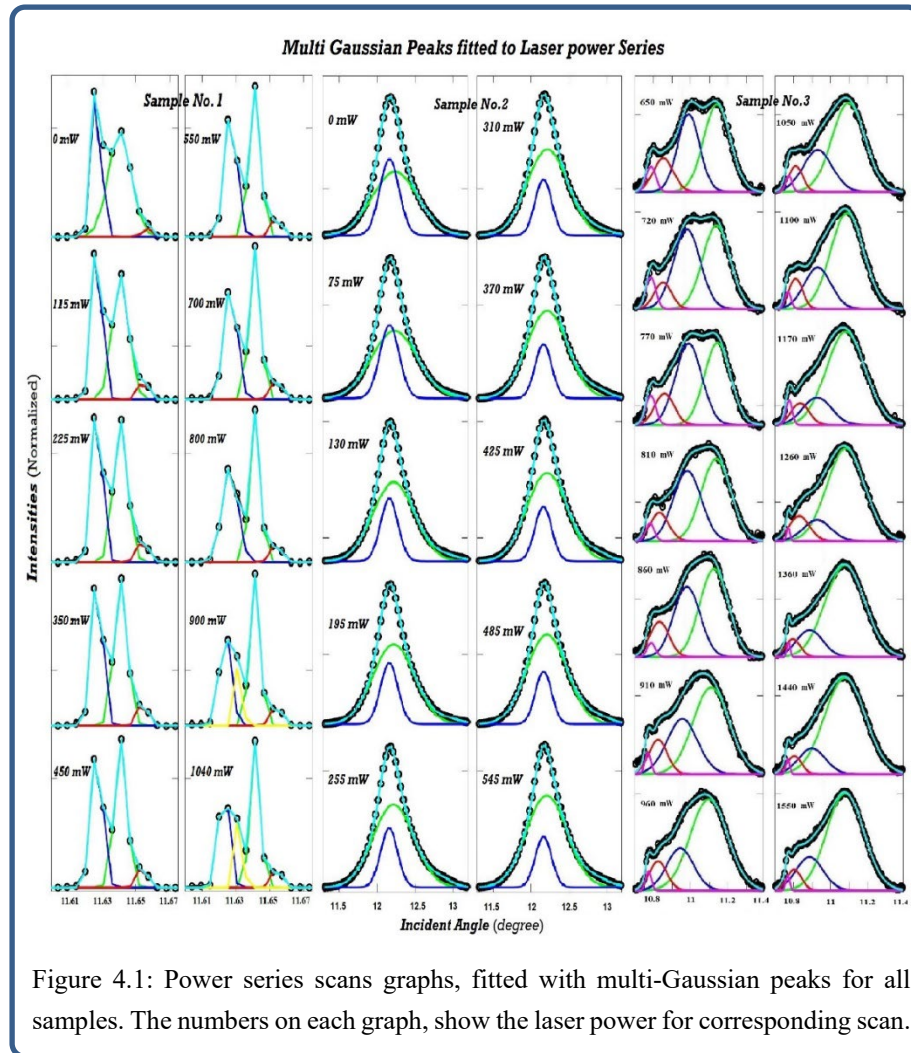
Table 4.1: Specification of three straight NWs samples

	Core Material	Core Diameter (nm)	Shell Material	Shell thickness (nm)	Total NWs thickness (nm)	NW lenght (μm)
Sample No.1	GaAs	200	-	0	200	1.55
Sample No.2	GaAs	150	-	0	150	1.55
Sample No.3	GaAs	100	In _{0.1} Ga _{0.9} As	30	160	2.89

First, we probed a small ensemble of NWs localized within a $400 \times 400 \mu\text{m}^2$ array on pre-patterned substrate by an x-ray beam of typical size $150 \mu\text{m} \times 200 \mu\text{m}$ in horizontal and vertical direction, respectively. Here we tested the tolerable laser power to avoid the beam damage at sample ²⁴. To achieve this goal, we increased the laser fluences stepwise without delays between laser pump and x-ray probe. Before that we aligned both laser and x-ray beams to guarantee maximum overlap at sample position. The maximum laser fluence which was 1600 mW, was used for further measurements. We measured the variation of NW lattice parameter along NW axis as function of delay time of the pico-second laser pulse, by probing the peak position of the 111 GaAs Bragg reflection. Rocking scans were performed using 9 kV X-ray in the vicinities of the [111] Bragg reflections probing thermal expansion along the NW growth direction. The scattered intensity distribution was collected using a two dimensional 100 k Pilatus detector. Due to the small incidence angle the x-ray footprint was enlarged along the beam direction (see Appendix 1).

The recorded data of samples 1, 2 and 3 are shown in Figure 4.1. It shows the evolution of 111 Bragg peaks as function of fluence. Whereas sample 2 shows one main peak sample 3 clearly shows several peaks. The peaks profiles have been de-convoluted by Gaussians marked by different colors. One may consider that the green peaks which corresponds to a larger Bragg angle belong to zinc-blende phase, whereas the blue curve measure the Wurtzite phase. Sample 2 shows only zinc-blende peaks, but sample 3 shows both peaks. The first curve of sample 2 was recorded without laser. It is considered as reference for the other scans.

Laser power series scans in both data collection campaign, show the almost equivalent role for X-ray scattered from both zinc blende (zb) and wurtzite (wz) structures for forming the whole scattered intensity at low laser power cases. By increasing the power of exciting laser, the intensity of zb phase increases of cost of that of the wz phase. This indicates that the energy of the laser beam induces a change in stacking sequence hexagonally closed-packed layers towards zb packing sequence. The



hexagonal layers oscillate as function of energy. If the energy of layers is large enough, they can jump from one stacking position to another stacking position. By increasing the laser power, the hexagonal closed packed stacking layers, get enough energy and change to zb packing sequence, therefore, show dominate role for zb structure in whole scattered graphs.

Tables 4.2 shows the results of lattice parameter variations as function of the laser power for sample No.3. The corresponding calculated results for samples No.1 and No.2 are presented in tables A4.3.1, A4.3.2 respectively. The last two tables are presented in appendix A4.3.

Table 4.2: Calculated results of laser power series for sample No.3

		<i>Zinc Blende</i>				<i>Wurtzite</i>			
	LP(mW)	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$
1	650	2.934	1.3303	51.455	1.153	2.881	1.1253	50.538	0.814
2	720	3.546	1.3572	62.184	1.177	3.717	1.3552	65.195	0.982
3	770	3.618	1.2907	63.446	1.116	3.575	1.3396	62.701	0.970
4	810	4.104	1.4606	71.965	1.265	4.482	1.4218	78.602	1.031
5	860	4.697	1.4112	82.377	1.223	4.945	1.3419	86.708	0.973
6	910	5.237	1.7952	91.840	1.555	5.496	1.5771	96.372	1.142
7	960	5.741	1.8517	100.672	1.604	6.065	1.3588	106.346	0.985
8	1050	6.515	1.6685	114.233	1.445	6.599	1.4977	115.696	1.085
9	1100	7.325	1.6444	128.423	1.424	6.919	1.3623	121.305	0.985
10	1170	8.423	1.9430	147.655	1.683	7.577	1.4850	132.835	1.075
11	1260	9.863	1.8903	172.870	1.637	8.217	1.4308	144.051	1.036
12	1360	10.871	1.9906	190.516	1.713	9.356	1.3868	163.987	1.003
13	1440	11.537	2.0433	202.173	1.767	10.476	1.3837	183.608	1.003
14	1550	12.041	1.8451	210.994	1.597	0.00662	1.3870	206.337	1.003

In all these tables, “ Δa ” and “ ΔT ” are the deviation values from reference values of lattice constant and temperature respectively, “ $\delta \Delta a$ ” and “ $\delta \Delta T$ ” are the measurement error of “ Δa ” and “ ΔT ”. One can considers that $\Delta a/a$ be the, axial strain (with respect to reference values) that the NWs endures, created by thermal expansion caused by laser beam.

Fig.4.2 shows the change of relative lattice spacing as function of laser floucnce for both zb and wz peaks of samples No.1, No.2 and No.3. In first data collection campaign, the lower laser power values had been applied and therefore the NWs expansion of corresponding samples (samples No.1 and No.2) are accordingly smaller rather than samples No.3.

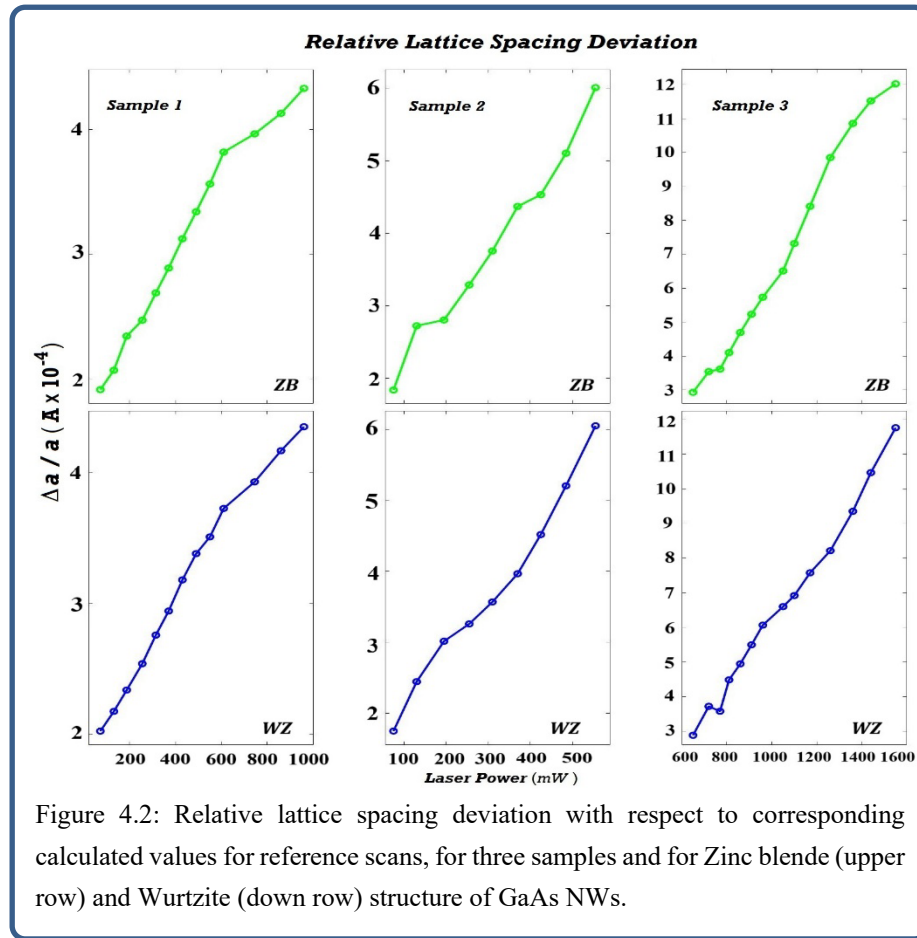
As expected the lattice spacing increases as function of laser floucnce. As it is clear in figure 4.2, the shape of the graph of changing the lattice spacing deviation of NWs as function of laser power, is almost same for three samples and they show the increasing of expansion by increasing the laser power, but this increasing occurs with different rate. The almost same

slope found for samples 2 and 3 correlates with almost same NW diameter of 150 and 160nm, respectively. On the other side the diameter of sample No.1 is 200 nm which correlated with smaller slope of lattice parameter variation. Therefore, one can conclude that NWs with smaller total thickness, undergo to more thermal expansion (with a steeper slope). With the other word, when the NWs have been irradiated with exciting laser power, the NWs with smaller total thickness, thermally expand faster and more (with greater rate) than the NWs with bigger total thickness.

Using the well-known relation between thermal lattice expansion and temperature

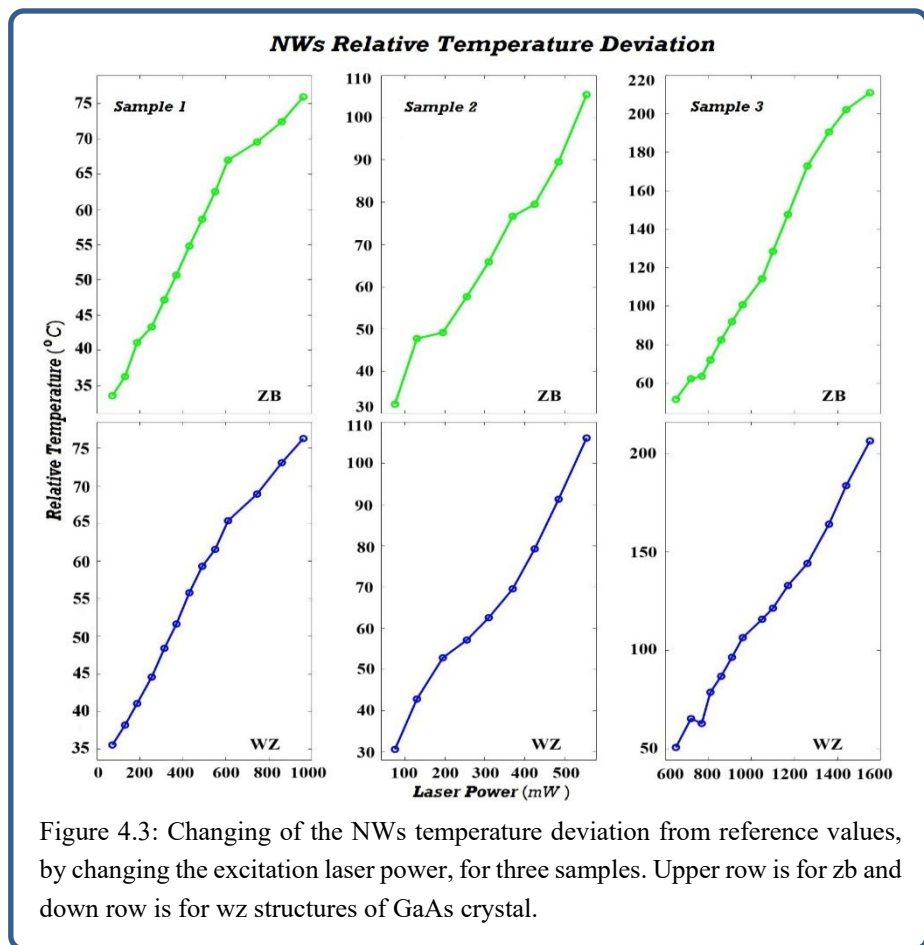
$$\Delta a / a = \alpha \Delta T \quad (4-1)$$

where α is the bulk thermal expansion coefficient $6.2 \cdot 10^{-6}/K$, the measured lattice expansion can be transformed into a NW lattice temperature



induced by the external laser pulse. This is shown in Figure 4.4 for both zb and wz phases of the NWs.

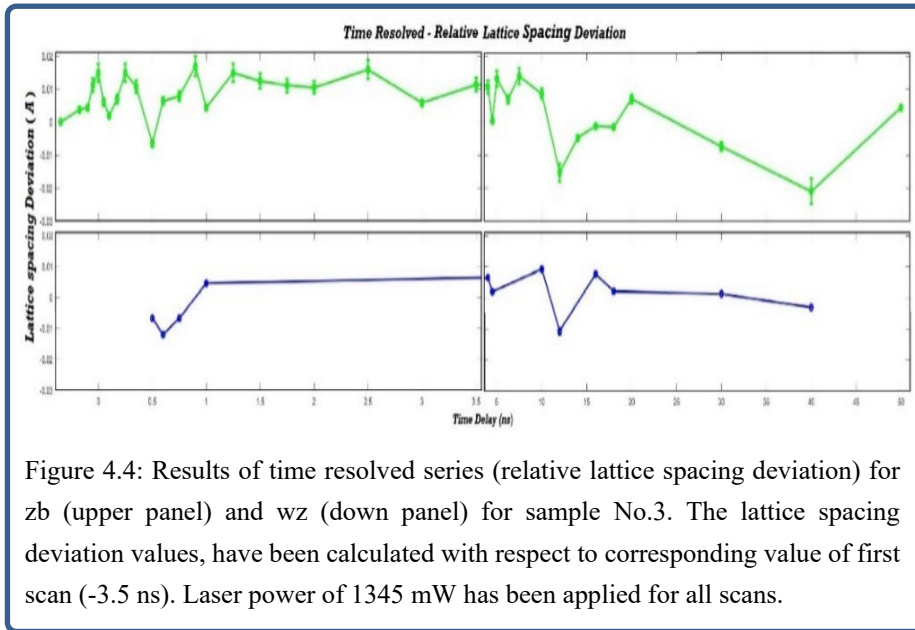
Rising of temperature of NWs caused by optical excitation of laser power, have been calculated by applying first harmonic approximation of thermal expansion equation for one dimension and using the thermal expansion coefficient of GaAs bulk lattice value. The values of temperature deviation, presented in tables 4.2, A4.3.1 and A4.3.2, are difference of temperature of NWs in certain laser power from temperature of corresponding reference. Figure 4.3 shows the rising of NWs temperature from reference values versus the laser power, for three samples and for Zinc blende (upper row) and Wurtzite (down row) structures. Temperature deviation shows same pattern of changing as the lattice constant deviation pattern. Therefore, one can concludes that the



temperature of the NWs with smaller total thickness, rising more and faster (with bigger rate) than the NWs with greater total thickness, if they have been irradiated with exciting laser power.

Data collection for time resolved series with time delay of probing X-ray pulses from exciting laser pulse between -450 ps to 1000 ps for first data collection campaign, and -0.5 ns to 50.0 ns for second data collection beam time (samples No.3), have been performed. The goals were to investigate the time dependency of the response of GaAs NWs to thermal excitation as well as investigation NWs behaviour after shutting down the laser pulse. Furthermore we want to investigate the thickness dependency of NWs behaviour during running and after shutting down the laser pulse. The results obtained for the first two samples (No.1 and No.2), showed no change in lattice constant deviation of NWs, by increasing delay time until 1.0 ns; This means that the time need for expanded NWs to react to shutting down the laser pulse is absolutely greater than 1.0 ns (See the results in tables A4.3.3 and A4.3.4 in appendix 3). In second data collection campaign, the time delay interval, has been expanded to 50.0 ns (for sample No.3). The fitted results for the sample No.3, has been presented in figure A4.2.1 (in appendix 2). This figure shows dominate role of Zinc blende structure in the overall graph formation, which is compatible with our results in laser power series scans with high laser power (Note that the laser power of 1345 mW has been applied for time resolved scans of sample No.3; see figure 4.1). This result strengthens our previous conclusion that at high energies of the excitation laser, the hexagonal closed pack stacking change to ZB stacking sequences.

The relative lattice constant deviation graphs (relative to lattice constant value of first scan, with -3.5 ns delay) versus time delay between laser and X-ray pulses for sample No.3 are shown in figure 4.4. This figure clearly shows pattern with irregular distortion. Therefore, one can conclude that the time needed for GaAs NWs to react to ending the laser pulse, and start returning back to its initial state, is obviously greater also than delay time of 50 ns.



4.3 Discussion

All scan series in both data collection campaign, either laser power series or time resolved series, clearly show two main peaks in X-ray scattered intensities. These peaks indicate the Bragg reflection of incoming X-ray from the [111] Bragg planes of Zinc blende (green peaks) and Wurtzite (blue peaks) structure of GaAs crystal.

All results of power series scans, show increasing of lattice spacing by increasing the power of exciting laser beam, which, as it has been expected, clearly show that the laser beam makes the NWs to expand thermally.

Laser power series scans in both data collection campaign, show the almost equivalent role to scatter incident X-ray by both Zinc blende and Wurtzite structures and forming the whole scattered intensity at low laser power cases; by increasing the power of exciting laser, the Zinc blende structure get dominate role and most scatter the X-ray beam; instead the Wurtzite structure gradually lose its role for forming the whole scattered graphs. This effect can be understood by changing the stacking sequence hexagonally closed-packed layers towards ZB packing sequence. When

the laser power increase, it transfer more energy to NWs, leads to changing the hexagonal closed packed stacking layers, to zb packing sequence, so the incident x-ray will scatter mostly by zb structure, therefore, figures show dominate role for zb structure in whole scattered graphs.

In addition to the value of excitation laser power, the NWs expansion, depend also to the total thickness of NWs. Rate of NWs expansion, changes by NWs total thickness, and increasing will occur with slower slope for thicker NWs (with smaller rate).

The time dependency response of Wurtzite and zinc-blende crystalline structure of GaAs NWs, is monitored by means of nanosecond time-resolved in-situ X-ray scattering in both data collection beam time. Despite of our initial goal to investigate the GaAs NWs response to laser pulse shutting down, the results do not show a change in lattice constant of NWs by passing the time delay until 50.0 ns. Therefore, one can conclude that the time needed to see any react of GaAs NWs to going down the laser pulse is much larger than 50.0 ns or smaller than 1 ps, and investigation of the time dependency response of GaAs NWs, and study the return behaviour of GaAs NWs, over the time, could been performed with wider time delay interval.

4.4 Appendix 4.1: Increasing the cross section of oblique laser beam on samples

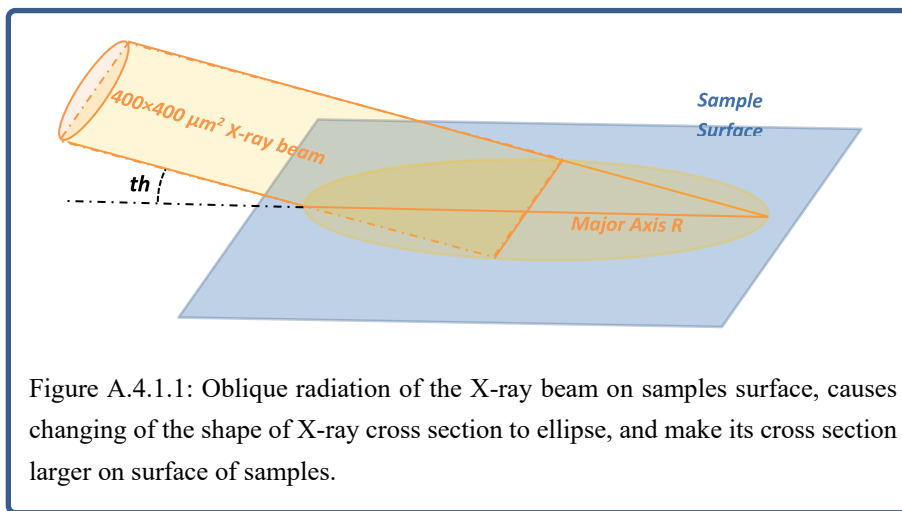
Let suppose an X-ray beam of $300 \times 300 \mu\text{m}^2$ spot size hit the sample with an angle of 11.2 degree with respect to the sample surface (11.2 degree is larger than all our incident angles measured -and presented in tables 4.1-4.4-). With these assumptions, cross section of X-ray beam will be circle with area of $7.0686 \times 10^4 \mu\text{m}^2$ and when hit the sample surface with angle around 11.2 degree it will form a ellipse on surface as it has been shown in figure 4.A.1.1 with minor axis of $300 \mu\text{m}$ and the major axis will be as

$$R = 300 \mu\text{m} / \sin 11.2 = 1544.56 \mu\text{m} = 1.54456 \text{ mm}$$

Which is absolutely bigger than the size of NWs array zone on our samples. The cross section of X-ray beam on sample surface (area of the ellipse has been formed on sample surface) is the product of the lengths of the semi-major axis and the semi-minor axis (which is unchanged and equal to horizontal beam size) and the constant π , therefore,

$$\sigma = \pi 1500 \mu\text{m} \times 772.28 \mu\text{m} = 363933.09 \mu\text{m}^2 = 0.363933 \text{ mm}^2$$

That means due to slanted radiation, the area covered by X-ray beam on the sample surface could be more than five time bigger as the perpendicular cross section (0.012 mm^2).



4.5 Appendix 4.2: Multi-Gaussian peaks fitted to scan's graphs

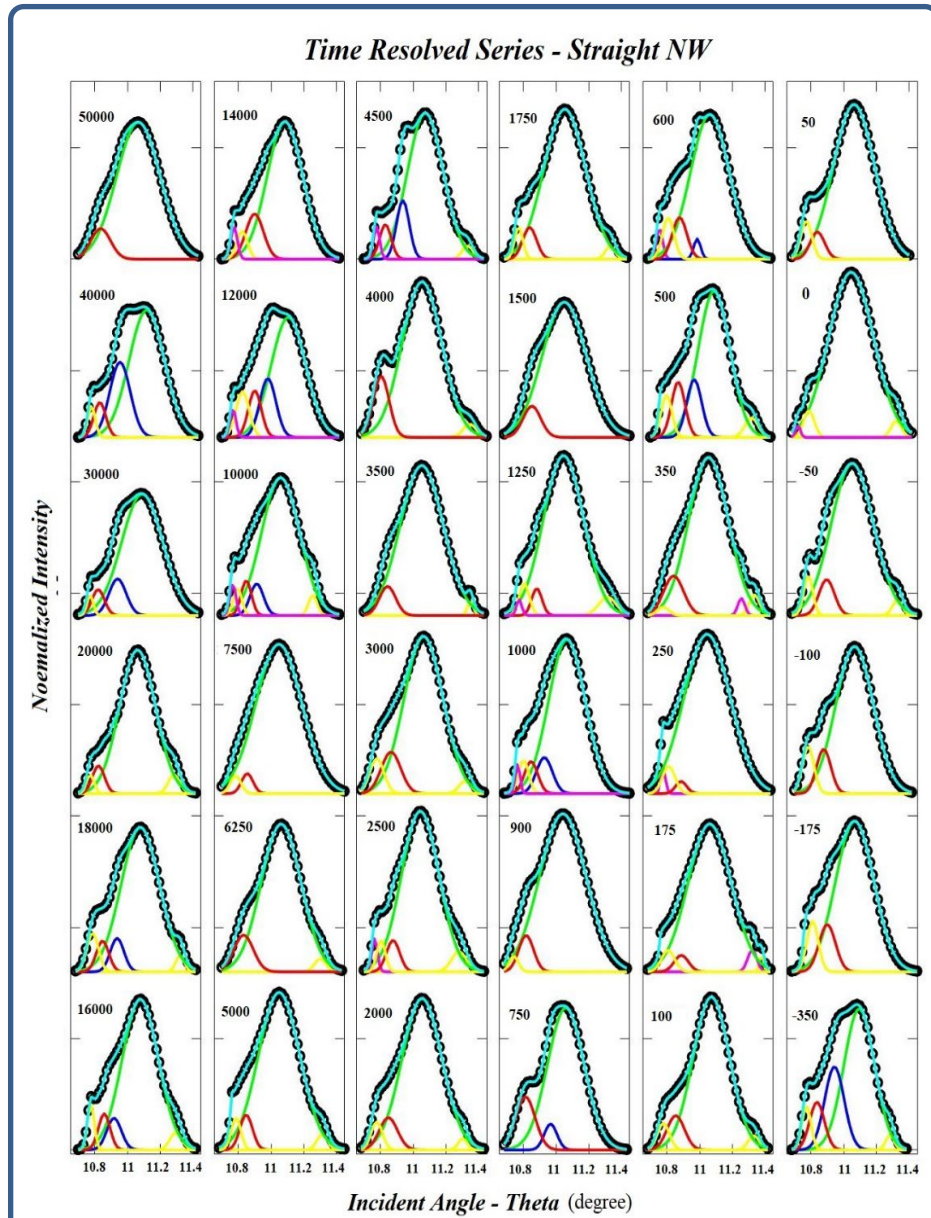


Figure A4.2.1: Multi-Gaussian peaks fit results for time resolved scans for sample No.3. The numbers on each scan, show the time delay between X-ray and laser beam in pico-second unit. The applied laser power for all these scans is 1340 mW.

4.6 Appendix 4.3: List of tables of calculated values

Table A4.3.1: Calculated results for laser power series scans for sample No.1

		<i>Zinc Blende</i>				<i>Wurtzite</i>			
	LP(mW)	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$
2	72	1.913	1.1378	33.551	1.101	2.026	1.0283	35.540	0.946
4	131	2.068	1.1442	36.276	1.107	2.177	1.1929	38.180	1.058
6	187	2.342	1.0449	41.080	1.011	2.340	1.0420	41.042	0.956
8	255	2.470	0.9872	43.318	0.955	2.541	1.2706	44.568	1.111
10	314	2.689	0.9135	47.158	0.883	2.759	0.9826	48.393	0.916
12	370	2.888	0.8526	50.659	0.824	2.943	1.2523	51.620	1.099
14	430	3.124	0.8109	54.785	0.784	3.181	1.1792	55.784	1.049
16	490	3.341	0.9712	58.590	0.938	3.381	1.1792	59.302	1.199
18	550	3.564	0.9712	62.497	0.938	3.509	1.2066	61.542	1.068
20	610	3.820	1.0449	66.984	1.009	3.727	1.2523	65.355	1.098
22	745	3.966	1.0641	69.546	1.028	3.929	1.2523	68.911	1.098
24	860	4.130	1.0641	72.433	1.028	4.167	1.1974	73.079	1.061
26	960	4.331	1.0641	75.954	1.028	4.350	1.1472	76.289	1.027

Table A4.3.2: Calculated results for laser power series scans for sample No.2

		<i>Zinc Blende</i>				<i>Wurtzite</i>			
	LP(mW)	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$
1	75	1.838	2.0419	32.240	0.348	1.747	0.7945	30.637	0.556
2	130	2.724	2.0083	49.190	0.366	2.443	0.8414	42.849	0.648
3	195	2.805	2.1137	65.899	0.368	3.013	0.8737	52.847	0.626
4	255	3.289	2.1250	79.517	0.329	3.258	0.9190	57.132	0.608
5	310	3.757	1.8987	105.455	0.376	3.567	0.9853	62.560	0.702
6	370	4.372	2.1713	76.675	0.367	3.966	1.0656	69.544	0.655
7	425	4.534	2.1170	79.508	0.377	4.518	1.2846	79.228	0.651
8	485	5.107	2.1780	89.551	0.376	5.206	0.9591	91.283	0.604
9	555	6.013	2.1818	105.432	0.358	6.052	0.8599	106.110	0.688

Time resolved series results

Table A4.3.3: Calculated values of time resolved series scans for sample No.3

		<i>Zinc Blende</i>				<i>Wurtzite</i>			
	<i>d</i> (ns)	$\Delta a/a$ E-5	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$	$\Delta a/a$ E-4	$\delta \Delta a$ E-5	ΔT (d)	$\delta (\Delta T)$
1	-0.35	0	0	0	0	0	0	0	0
2	-0.175	0.666	0.9140	11.680	0.020				
3	-0.1	0.774	0.9016	13.573	0.024				
4	-0.05	2.017	1.0137	35.308	0.061				
5	0	2.683	1.0833	46.942	0.081				
6	0.05	1.080	0.9822	18.933	0.033				
7	0.1	0.342	0.8713	6.000	0.010				
8	0.175	1.260	1.0327	22.084	0.038				
9	0.25	2.683	1.1164	46.942	0.081				
10	0.35	1.927	0.9548	33.735	0.059				
11	0.5	-1.152	0.7534	-20.240	-0.035	-1.201	3.7080	-21.120	-0.204
12	0.6	1.152	0.9264	20.194	0.035	-2.139	1.7191	-37.667	-0.364
13	0.75	1.404	0.8778	24.605	0.043	-1.201	3.1672	-21.120	-0.204
14	0.9	3.043	1.1242	53.223	0.092				
15	1	0.792	0.8756	13.888	0.024	0.793	4.0635	13.898	0.134
16	1.25	2.683	0.9696	46.942	0.081				
17	1.5	2.233	1.0647	39.083	0.068				
18	1.75	1.981	1.0023	34.679	0.060				
19	2	1.891	0.9575	33.106	0.057				
20	2.5	2.863	0.9054	50.083	0.087				
21	3	1.044	0.9353	18.302	0.032				
22	3.5	2.035	1.0338	35.623	0.062				
23	4	1.909	0.9576	33.420	0.058	1.159	1.7651	20.299	0.196
24	4.5	0.054	0.8510	0.948	0.002	0.339	3.1899	5.943	0.057
25	5	2.359	0.9928	41.284	0.072				
26	6.25	1.242	0.9550	21.769	0.038				
27	7.5	2.503	1.1105	43.799	0.076				
28	10	1.530	0.9116	26.810	0.047	1.631	3.4123	28.528	0.276
29	12	-2.773	0.8140	-48.782	-0.085	-1.911	3.9980	-33.645	-0.325
30	14	-0.882	0.8476	-15.492	-0.027				
31	16	-0.234	0.8610	-4.108	-0.007	1.353	3.7050	23.682	0.229
32	18	-0.288	0.9159	-5.056	-0.009	0.365	3.4174	6.400	0.062
33	20	1.260	0.8640	22.084	0.038				
34	30	-1.332	0.9780	-23.407	-0.041	0.224	4.3028	3.932	0.038
35	40	-3.781	0.8323	-66.589	-0.116	-0.552	5.1339	-9.692	-0.094
36	50	0.774	1.0473	13.573	0.024				

*Investigation of Be Dopants Diffusion Along
GaAs NW by Fermi Energy Level Monitoring**

5.1 Introduction

The feasibility of semiconductor nanowires has been demonstrated for numerous technically and scientifically interesting devices, such as Field Effect Transistors (FETs), single-electron transistors, or spin-orbit based qubits.²³ Formation of heterojunctions in nanowires usually requires doping with donors or acceptors. Doping in Si nanowires has been demonstrated and did fabricate photovoltaic devices, single-quantum-dot, light-emitting diodes, and Tunneling Field Effect Transistors.²³ However, the control of the electrical properties of nanowires through doping, more specifically in axial and/or radial dopant distribution, is a necessity for the development of the field. So a local probe of the electrical properties of nanowires that provides information on morphology and its dependence on growth mechanisms, would be very useful.²⁴ In this way, the control of the doping in nanowires is of fundamental importance for the implementation of nanowires-based devices.

In Molecular Beam Epitaxy (MBE), doping is achieved by adding a selected impurity in the vapor phase during growth. Incorporation was found to depend on the orientation of the substrate surface, on the growth temperature and on the As/Ga flux ratio employed during growth. GaAs nanowires are often grown by molecular beam epitaxy using Au or Ga nanoparticles to promote the one-dimensional (axial) growth of the nanowire material following the Vapor-Liquid-Solid (VLS) mechanism.²⁵

* This chapter is a paper draft prepared with the collaboration and revisions of our colleagues in Elatra (Italy) and has not yet been submitted.

Local variations on the nanoscale might induce significant changes in nano-device performance. The importance of spatial control of dopant concentration for understanding electrical nanowire properties was reported by Ruqaiya Al-Abri (reference No. 26) probed by high-throuput spectroscopy. However, many questions are still open. Spatially resolved X-Ray Photoelectron Spectroscopy (XPS) is a method to provide such information, at least, for doping distribution close below the surface. Considering the physics of surface depletion the local shift of the surface Fermi level can be associated with the enhancement or depletion of doping atoms close to the surface.²⁵ The method has been applied for the analysis of Be dopant distribution in GaAs nanowires using spatially resolved X-Ray Photoelectron Spectroscopy.

Monitoring of the doping in NWs has been achieved by means of atom probe tomography²⁷, which has been successfully applied to map the dopant distribution within a single semiconductor NW body²⁸, and by quantitative scanning photocurrent microscopy.²⁵ In-situ doping in compound semiconductor nanowires has been investigated in reference No. 29 using Metal-Organic Vapor-Phase Epitaxy (MOVPE) growth scheme. P- and n-doping in InP, GaAs, and ternary materials such as $\text{Ga}_x\text{In}_{1-x}\text{P}$ could be demonstrated and was used to compose p-i-n doped InP nanowire arrays. The doping mechanism of compound semiconductor nanowires grown via vapour-liquid-solid growth mode has been reviewed in reference No. 30 including in-situ and ex-situ doping methods and the resulting properties.

5.2 Experimental Tasks *

5.2.1 Experimenal Technique

Common tools to study the morphology and structure of nanowires are scanning and transmission electron microscopy. Whereas Scanning Electron Microscopy gives fast access to the size and shape of nanowires and their distribution on the surface, Transmission Electron Microscopy can be used to map the crystal structure of selected nanowires or chemical compositions and strains along interfaces.^{31, 32, 33}

The same technique as explain by Majid Kazemian Abyaneh ³⁴ is applied for the current part. Here GaAs nanowires doped with Be of different concentration have been investigated. The experiment has been performed at synchrotron Elettra²⁴ using photoemission spectro-microscopy.* The experimental results are complemented by theoretical simulations of the carrier profile, taking into account the presence of electronic surface states and quantifying the impact of carrier depletion at the nanowire surface. This combined approach allows to determine the effect of the incorporation of Be dopants in GaAs nanowires, in the resulting core-shell structures and axial junctions. The method also revealed the strong dependence of the resulting doping on the morphology of the single nanowire (orientation, shell thickness). This approach can be easily applied to other nanoscale objects, allowing the direct observation of how doping (or junctions, or adsorbates,...) may locally affect the position of the Fermi level at the surface, which is a crucial factor in several application fields, such as photovoltaic and photocatalysis.²⁵

Spatially resolved X-ray photoelectron spectroscopy measurements were performed with the scanning photo electron spectro-microscopy at the ESCA microscopy beamline of the Elettra synchrotron light facility. A schematic layout of the apparatus is shown in Figure 5.1a). scanning photo electron spectro-microscopy uses a direct approach to obtain spatial resolution; i.e., the incoming x-ray beam is focused down to a diameter of 100 nm using Fresnel zone plate optics.

Scanning Photo-Electron Microscopy (SPEM) has already been used in the study of quasi one dimensional nanostructures such as carbon nanotube bundles or some nanowires, to probe with spatial resolution the surface chemistry and the transport properties of the nanostructures.

The overall uncertainty on the measured Ga3d peak position has been estimated to be 0.1 eV. For the measures presented here, the photon energy has been kept at 500 eV. After scanning photo electron microscopy

* Due to restrictions during the pandemic, the experiments have been executed remotely

mapping of the sample, Ga 3d and As 3d core level emission was recorded at different positions along single nanowires. After the scanning photo electron microscopy measurements, samples were observed ex-situ by scanning electron microscopy (SEM, Zeiss Supra 40 field-emission apparatus) and each nanowire measured by scanning photo electron microscopy was localized and characterized by high resolution SEM images.²⁵ The lower panels of Figure 5.1, shows SPEM images (Figure 5.1.b) and representative Ga 3d spectra, recorded from selected positions on two neighboring nanowires (Figure 5.1.c).

5.2.2 Samples Description

In this part five GaAs samples have been analyzed which are four Beryllium doped ones grouped into two series and one un-doped sample used as a reference (sample No.5). Both series have been measured in two different experimental campaigns. All were grown by Ga assisted molecular beam epitaxy onto Silicon (111) substrate covered by native oxide. nanowires of the first group are doped with Be of $2 \times 10^{17} \text{ cm}^{-3}$ and $1 \times 10^{18} \text{ cm}^{-3}$ along the whole nanowire length, sample No.1 and 2, and are

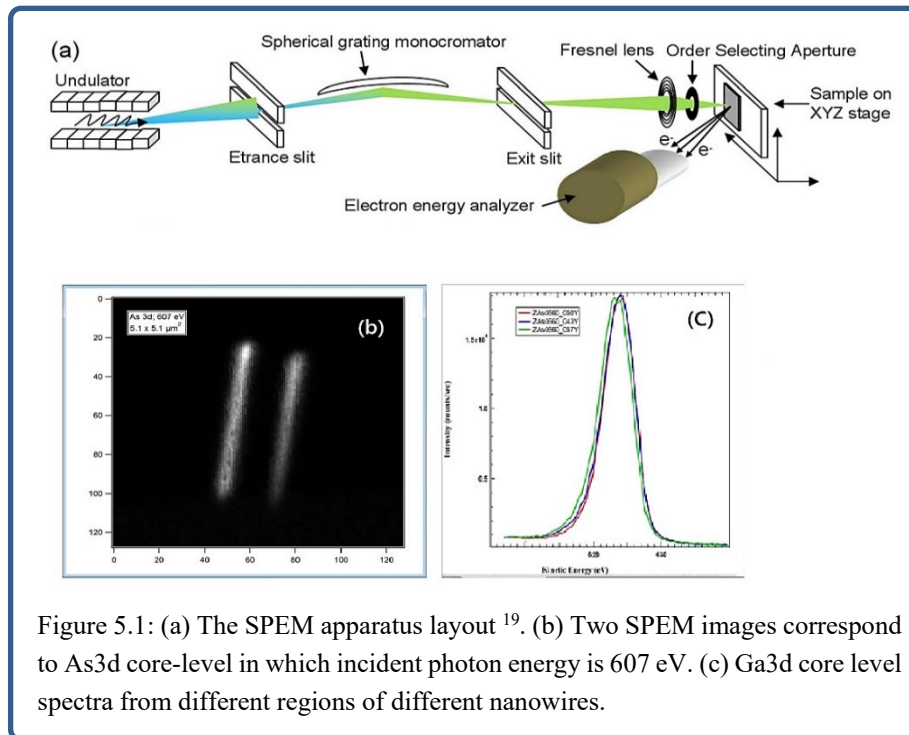


Figure 5.1: (a) The SPEM apparatus layout ¹⁹. (b) Two SPEM images correspond to As3d core-level in which incident photon energy is 607 eV. (c) Ga3d core level spectra from different regions of different nanowires.

covered by an $\text{Al}_{0.1}\text{Ga}_{0.9}\text{As}$ shell of 10 nm thickness. Nanowires of second group have a Be concentration of $1 \times 10^{19} \text{ cm}^{-3}$ and $5 \times 10^{19} \text{ cm}^{-3}$ (samples No.3 and sample No.4 respectively). Here molecular beam epitaxy growth is performed in three steps: first, a GaAs core is grown for 300 s by vapor liquid solid mechanism followed by an uniformly thick axial segment of Be doped GaAs grown by 800s and ending with pure GaAs segment grown by 200 s all at 630 °C. The doped region is marked by thin AlGaAs discs, as seen in Figure 5.2. For more details about sample growth, please refer to references.^{35, 36}

Application of spectro-microscopy requires some preliminary samples preparation. First the samples were cut in such a way that free standing nanowires appear close to the cleavage plane in order to access the nanowire by the x-ray beam in the direction nearly perpendicular to the nanowire length axis. Second, the samples were cleaned by Ar^+ plasma in order to remove oxides and impurities from the nanowire surface. Finally, the sample has to be heated in H atmosphere to remove remaining oxide. The final step was performed for one hour at 400 °C. Next, the samples

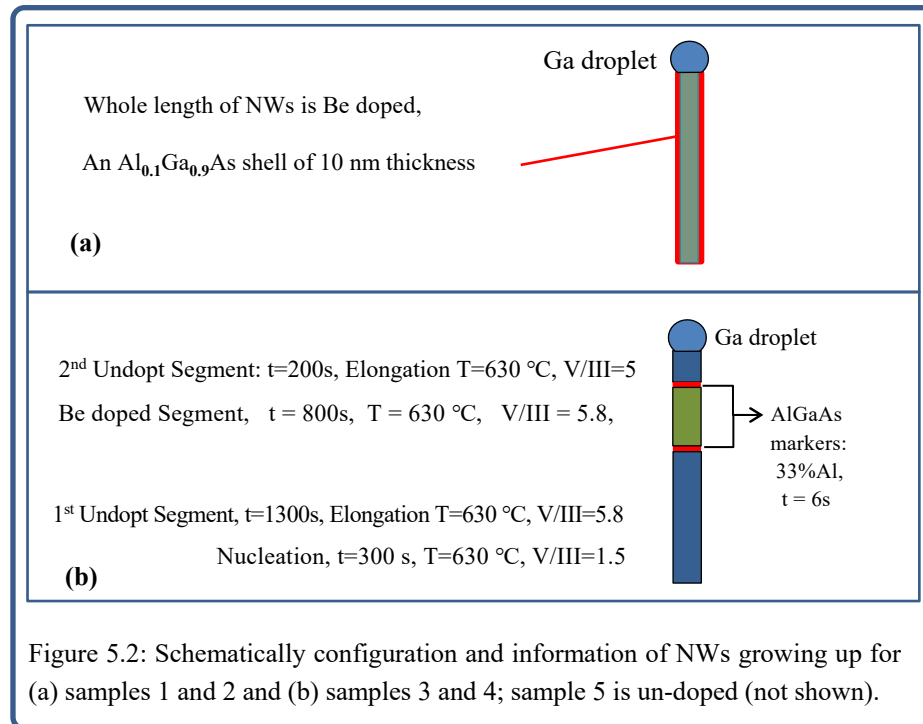


Figure 5.2: Schematically configuration and information of NWs growing up for (a) samples 1 and 2 and (b) samples 3 and 4; sample 5 is un-doped (not shown).

were transferred into the experimental chamber and aligned with nanowire length axis almost perpendicular to the incoming x-ray beam in two configurations in which the tip of nanowire be up or down.(see Figure 5.3).

5.2.3 Measurement Description

The NWs were imaged by photoemission electron microscopy and the differences in the doping level of the different segments along the NW axis were clearly resolved by means of the observed variations in the secondary electron emission intensity. In this part, we used synchrotron radiation photoemission spectro-microscopy to monitor with a lateral resolution of 120 nm, the position of the Fermi level E_F within the bandgap at the surface of GaAs NWs, doped with Be and grown up with and without Ga-assisted molecular beam epitaxy under different growth conditions. The data are analyzed according to a model recently proposed by Chia ³⁷, which takes into account surface states and the related pinning of the Fermi level as a function of the NW diameter, the free-carrier density and the electronic surface state density. The results of the simulations are in good agreement with the experiment for reference samples of NWs grown with constant dopant flux, and then our combined approach allowed us to quantitatively investigate the nature of doping in more complex structures, including axial homojunctions, and core-shell radial junctions.

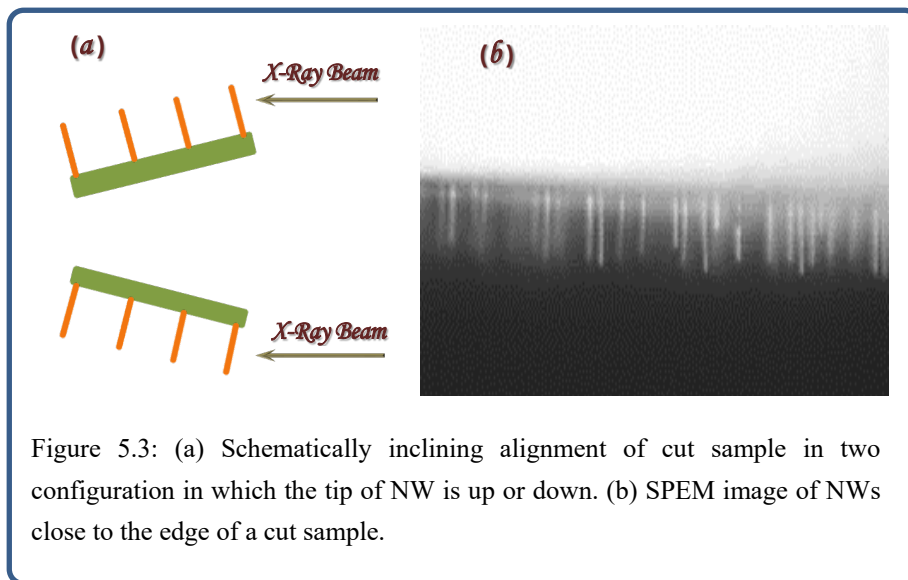


Figure 5.3: (a) Schematically inclining alignment of cut sample in two configuration in which the tip of NW is up or down. (b) SP-PEM image of NWs close to the edge of a cut sample.

The photoelectrons were collected with a SPECS-PHOIBOS 100 hemispherical analyzer and detected by a 48-channel electron detector.³⁴ Analyzer pressure was down to 4×10^{-9} mbar. Scanning photoelectron microscope operates in two modes: imaging and spectroscopy. In the first mode, the signal of NW is mapped by synchronized scanning with respect to the focused photon beam, and photo-emitted electrons are collected at a fixed kinetic energy. The second mode is X-ray photoelectron spectroscopy line profile spectrums from a submicron spots, obtained by moving the beam in steps along each NW. Nanostructures smaller than 50 nm have been mapped and characterized by microprobe X-ray photoelectron spectroscopy with an overall spectral resolution better than 200 meV.³⁴ As reference, the signal of an Au sample was routinely recorded used to calibrate the energy scale with respect to E_F by setting the value of 84.00 eV for the Au 4f_{7/2} emission.²⁵

As first step, Be dopant distribution across the nanowires population on a given sample has been investigated. Here the Binding Energy (BE) of the core level spectra of three nanowires on the same sample, gotten by using second mode data collection (X-ray photoelectron spectroscopy line profile spectrums), have been investigated. The core energy level spectrums of several nanowires in the same sample, show a mean core level shift of about 0.7 eV for Ga 3d and 0.5 eV for As 3d compared to the corresponding energy levels of the un-doped reference sample. This result has been observed for both spin-orbit interaction lines. Moreover, depending on the doping concentration, the values of core energy level for the measured NWs of one sample are different and show inhomogeneous dopant distribution across the nanowires population on a given sample that is compatible with M. Fanetti²⁵ who measured Si doped GaAs nanowires. Although here the values are not so large as Fanetti reported and are about 0.3 eV. However, this effect is still a challenge for having an absolute control on growing doped nanowires as well as for having exact information about doping mechanism. Figure 5.4 shows this effect (core energy level deviation) for three nanowires of sample No.3.

All lines display the double line features originated by spin orbit splitting of the emission lines into $3d^{5/2}$ and $3d^{3/2}$, as expected. It clearly express the line shift towards smaller binding energies for the doped samples compared to the reference where the amount of peak shift increases with increasing doping concentration.

As second step, one pair of SPEM images of nanowires from each sample have been investigated; Each pair contains one scanning photo electron microscopy image of nanowire of Ga 3d and one scanning photo electron microscopy image of As 3d. In this step the samples were scanned in the imaging mode (first mode data collection) using by X-ray beam with incident energy of 648.3 eV for sample No.3 and sample No.4 and energy of 650 eV for sample No.1 and sample No.2 and beam size of 300 nm in direction almost parallel to the substrate recording the Ga 3p and As 3p signals to identify single nanowires. Since the nanowires were grown on silicon substrate both signals provide exclusive information about the

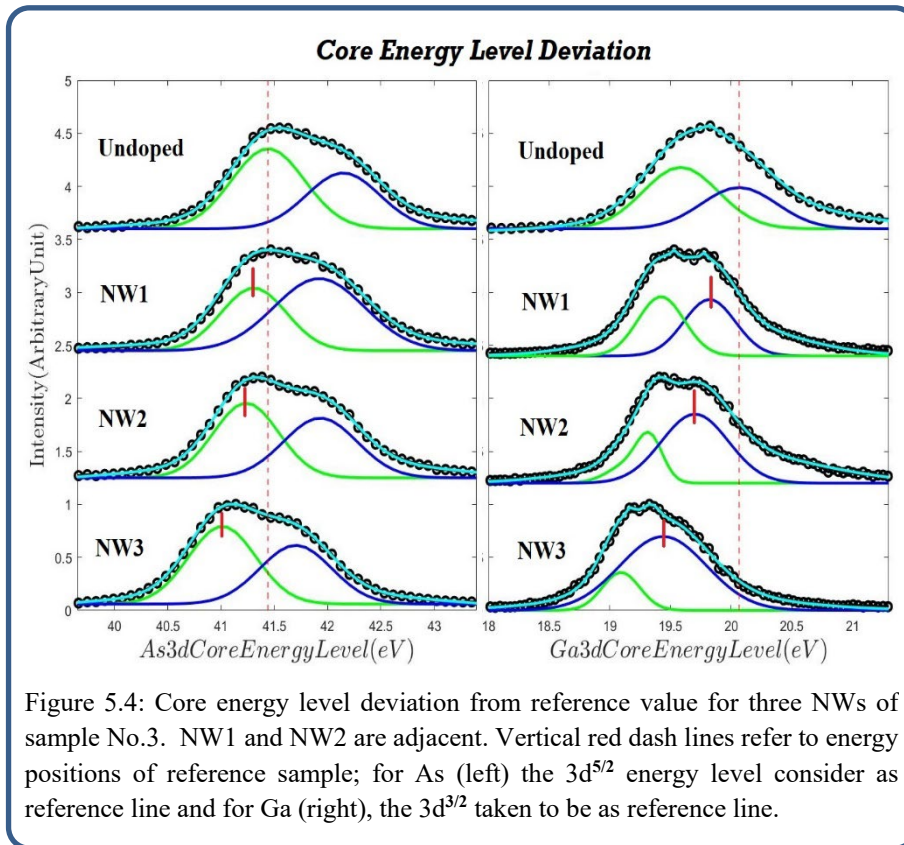


Figure 5.4: Core energy level deviation from reference value for three NWs of sample No.3. NW1 and NW2 are adjacent. Vertical red dash lines refer to energy positions of reference sample; for As (left) the $3d^{5/2}$ energy level consider as reference line and for Ga (right), the $3d^{3/2}$ taken to be as reference line.

nanowire positions. Figure 5.5 shows the scanning photo electron microscopy images of nanowires. The upper row shows the As 3d scanning photo electron microscopy images for sample No.1 (Figure 5.5a) to sample No.4 (Figure 5.5d) and second row shows the corresponding images for Ga 3d, respectively. Whereas for samples No.1, sample No.2 and sample No.4 a single nanowire could be identified, sample No.3 did show a region containing two nanowires close by.

Following Einstein equation,

$$E_b = E_i - E_m , \quad (5.1)$$

the peak shift between the bulk emission line E_i and the measured peak E_m is related to the bonding energy E_b .

Since the binding energy of Ga 3d doublet are proportional to those of the As 3d ones, we further follow the behavior of the Ga 3d^{5/2} line. In order to achieve detailed local information about Be distribution in whole length of nanowires, the samples were probed using a focused beam of 300 nm diameter with step wide of 10 nm.

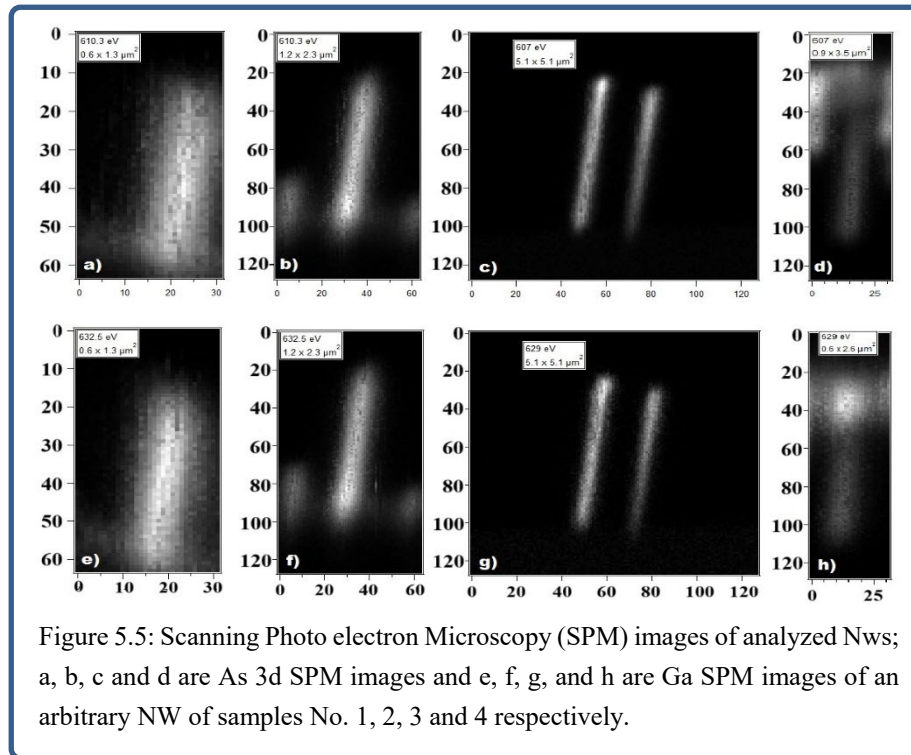
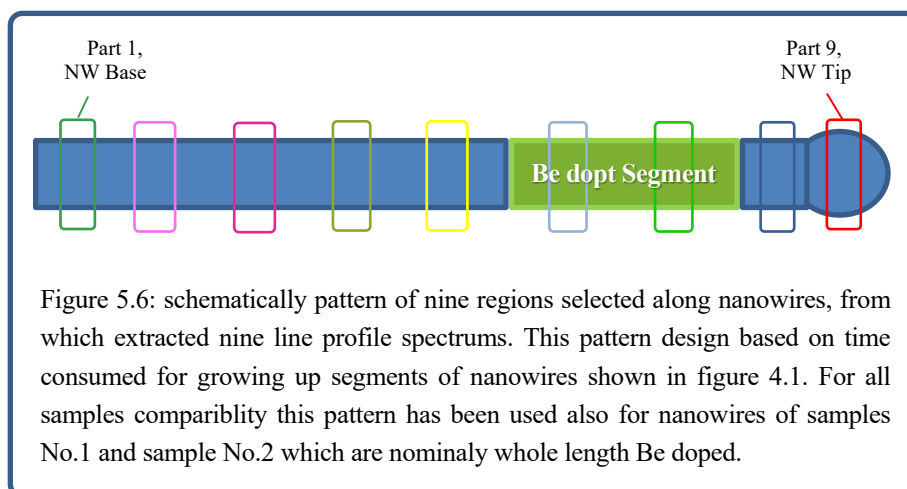


Figure 5.5: Scanning Photo electron Microscopy (SPM) images of analyzed Nws; a, b, c and d are As 3d SPM images and e, f, g, and h are Ga SPM images of an arbitrary NW of samples No. 1, 2, 3 and 4 respectively.



In order to achieve detailed local information about Be distribution in whole length of NWs, nine line profiles have been extracted from nine different regions along scanning photo electron microscopy image of NWs. Due to special dopants distribution of sample No.3 and sample No.4, and based on time consumption for growing up each segment of these samples (see Figure 5.1) a special pattern for choosing extractable regions, has been used. Figure 5.6 schematically show the pattern of nine regions, NWs divided to them and line profile spectrums have been extracted from them.

The whole length of nanowires of four samples were subdivided into nine different but not overlapping segments along nanowire length axis, using same pattern; and has been analyzed in terms of their spectral distribution independent of their individual length. Despite of different nanowires length of four doped samples, relative (to whole length of individual nanowire) position of each part in every nanowire, is the same as the relative position of similar part in other nanowires. Then from each of these nine segment, one spectra from image, have been extracted and analyzed. i.e. whole length of nanowires of all four samples have been analyzed (see Figures. 5.9 and 5.10). Figure 5.7 shows nine divided parts of Ga 3d and As 3d scanning photo electron microscopy image of an arbitrary nanowire of sample No.2, together with their nine extracted line profile spectrums as an example.

5.3 *Analytical Model*

To better understand the extent of surface depletion effect, and to calculate the expected E_F position at the nanowires surface, simulations have been performed in the continuous field approximation according to a model, by solving Poisson's equation. The model presented by Schmidt³⁸.

An earlier model provides a solution to Poisson's equation along with comprehensive analytical expressions for various nanowire parameters; however, it fails to satisfy the boundary conditions in scenarios where the nanowire is not fully depleted. A subsequent model, proposed by Simpkins³⁹, offers a complete solution to Poisson's equation that satisfies all boundary conditions, yet it is not applicable in the case of full depletion and does not incorporate of surface state density into the final solution. Therefore, there remains a need for a model that is both accurate and comprehensive in describing surface depletion. In the present work, nanowire surface depletion is addressed through the solution of Poisson's equation in cylindrical coordinates. Invoking the symmetry of a long nanowire, Poisson's equation can be simplified to an ordinary differential equation in r , the radial distance

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} = -\frac{\rho}{\epsilon}, \quad (5.2)$$

where ψ is the electric potential, ρ is the net bulk charge density, and ϵ is the permittivity of GaAs. In general, the solution to this equation is given by³⁹

$$\psi(r) = -\frac{\rho}{4\epsilon} r^2 + C_1 \ln(r) + C_2, \quad (5.3)$$

where C_1 and C_2 are constants. To find C_1 and C_2 , both Neumann and Dirichlet boundary conditions must be imposed on Equation (5.3)

$$\psi(r_q) = \psi_0, \quad (5.4)$$

$$\left. \frac{d\psi(r)}{dr} \right|_{r=r_q} = 0, \quad (5.5)$$

where r_q is the radius of the quasi-neutral core region of the nanowire as shown in Figure 5.8 and ψ_0 is the potential at the center of the nanowire

(along the nanowire axis). Equation (5.4) merely states that at $r = r_q$, the potential is given by the constant ψ_0 , as is evident from the equipotential quasi-neutral region between $r = 0$ and $r = r_q$ in Figure 5.8. Equation (5.5) merely states that at $r = r_q$, the radial component of the electric field is zero, which is a necessary requirement at steady state.³⁷

5.3.1 Partially Depleted Regime: $r_q > 0$

By substituting the boundary conditions (5.4) and (5.5) into Equation (5.3), C_1 and C_2 can be found and subsequently yield

$$\psi(r) = \frac{\rho r_q^2}{2\epsilon} \left[-\frac{r^2}{2r_q^2} + \ln\left(\frac{r}{r_q}\right) + \frac{1}{2} \right] + \psi_0, \quad (5.6)$$

Upon close examination, it can be immediately seen that this solution does not hold for a fully depleted nanowire (i.e., $r_q = 0$) since $\ln(r/r_q)$ term is undefined. This special situation in the fully depleted regime where $r_q = 0$ will be analyzed later. However, Equation (5.6) gives a general expression of the potential in a nanowire in the partially depleted regime where $r_q > 0$. To explicitly find this potential, ρ , ψ_0 , and r_q must be found. An expression for ρ will first be found.³⁷

a. Determination of ρ

In general, the charge density in the nanowire, $\rho(r)$, can be given as

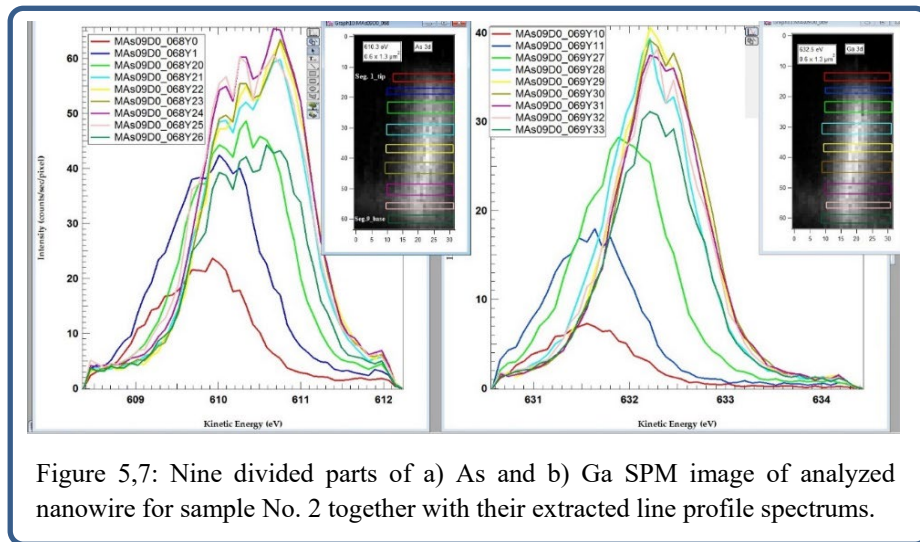


Figure 5.7: Nine divided parts of a) As and b) Ga SPM image of analyzed nanowire for sample No. 2 together with their extracted line profile spectrums.

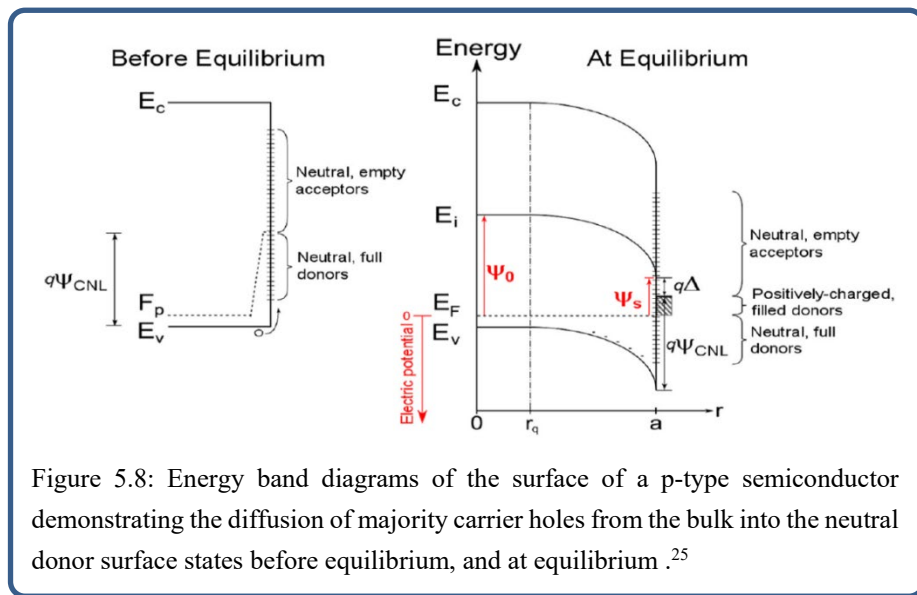
$$\rho(r) = q[p(r) - n(r) + N_D^+ - N_A^-] , \quad (5.7)$$

where q is the elementary charge, $p(r)$ is the free hole carrier density, $n(r)$ is the free electron carrier density, N_D^+ is the ionized donor doping density and N_A^- is the ionized acceptor doping density. In the quasi-neutral region of the nanowire between $r = 0$ and $r = r_q$, $n = N_D^+$ and $p = N_A^-$, thus making $\rho = 0$. Conversely, in the Space Charge Region (SCR) between $r = r_q$ and $r = a$ of an n-type nanowire (i.e., $n, N_D^+ \gg p, N_A^-$), the full depletion approximation (i.e., $n \ll N_D^+$) and complete ionization assumption (i.e., $N_D = N_D^+$) result in a space charge region charge density of $\rho = qN_D$ (With a similar approach for a p-type NW one can easily get $\rho = -qN_A$ or as we will use in the rest $\rho = -qN_a$). Therefore, the overall charge density in the nanowire can be written as

$$\rho = \begin{cases} 0 & \text{for } 0 < r < r_q \\ -qN_a & \text{for } r_q < r < a \end{cases} , \quad (5.8)$$

where a is the radius of the GaAs NW. Substituting Eq. (5.8) into Eq. (5.6) gives

$$\psi(r) = \begin{cases} \psi_0 & \text{for } 0 < r < r_q \\ \psi_0 - \frac{qN_a r_q^2}{2\epsilon} \left[-\frac{r^2}{2r_q^2} + \ln\left(\frac{r}{r_q}\right) + \frac{1}{2} \right] & \text{for } r_q < r < a \end{cases} \quad (5.9)$$



6. Determination of ψ_0

Typically, the Boltzmann approximation can be used to calculate the Fermi-level position based on the free carrier density. However, for high doping concentrations, as is typically the case for many nanowire device applications, the Boltzmann approximation is not entirely valid at all radii. In general, the free electron and hole concentrations are given by

$$n(r) = \frac{2}{\sqrt{\pi}} N_c F_{1/2}(\eta_F) , \quad (5.10)$$

$$p(r) = \frac{2}{\sqrt{\pi}} N_v F_{1/2}(\eta'_F) , \quad (5.11)$$

where $F_{1/2}(\eta)$ is the Fermi-Dirac integral given by

$$F_{1/2}(\eta) = \int_0^\infty \frac{x^{1/2}}{\exp(x - \eta) + 1} dx , \quad (5.12)$$

$$\eta_F = \frac{E_F - E_C}{kT} = \frac{q\psi(r) - E_g/2}{kT} , \quad (5.13)$$

$$\eta'_F = \frac{E_V - E_F}{kT} = \frac{-(q\psi(r) + E_g/2)}{kT} , \quad (5.14)$$

where N_c is the effective density of states in the conduction band, N_v is the effective density of states in the valence band, E_g is the energy bandgap, k is the Boltzmann constant, and T is the temperature. The Fermi-Dirac integral cannot be solved analytically, but can be calculate numerically. Since $r_q > 0$, the center of the nanowire is part of the quasi neutral region of the nanowire and $\rho = 0$. If the nanowire is doped with p-type element and complete ionization is assumed, then we have

$$\frac{2}{\sqrt{\pi}} N_v F_{1/2}(\eta'_{F0}) = N_a , \quad (5.15)$$

where η'_{F0} is the value of η'_F in the center of the nanowire and one can write

$$\eta'_{F0} = \frac{-(q\psi_0 + E_g/2)}{kT} , \quad (5.16)$$

Using equations (5.12), (5.14), (5.15) and (5.16) the values of ψ_0 will have been determined. At this point, with ψ_0 and ρ determined, an expression for r_q is the last requirement to provide a full expression of $\psi(r)$.²⁵

3. Determination of r_q

r_q can be found by examining the potential at the surface $\psi_s = \psi(r = a)$. According to Equation (5.9),

$$\psi_s = \frac{-qN_a r_q^2}{2\epsilon} \left[-\frac{a^2}{2r_q^2} + \ln\left(\frac{a}{r_q}\right) + \frac{1}{2} \right] + \psi_0, \quad (5.17)$$

From this equation, r_q (or correspondingly the depletion width, defined as $w = a - r_q$) can only be found if ψ_s is known. ψ_s can be calculated precisely and independently by examining the surface charge and invoking charge neutrality. The Charge Neutrality Level (CNL) of GaAs is $\psi_{\text{CNL}} = 0.53 \text{ V}$.³⁷ If a variable Δ is defined as $\Delta = E_g/2q - \psi_{\text{CNL}} = 0.18 \text{ V}$, the surface charge will then be given by

$$Q_{it} = -q \int_{E_i - q\Delta}^{E_i + q\psi_s} D_{it} dE, \quad (5.18)$$

where D_{it} is the density of interface states at the GaAs/air interface. Assuming that D_{it} is uniform between $E_i - q\Delta$ and $E_i + q\psi_s$,

$$Q_{it} = -q^2 D_{it} (\psi_s + \Delta), \quad (5.19)$$

Charge neutrality states that the sum of all bulk and surface charges in the system, is zero

$$\pi(a^2 - r_q^2)\rho_g + 2\pi a Q_{it} = 0, \quad (5.20)$$

Substituting Equation (5.19) into Equation (5.20) gives

$$\psi_s = -\frac{qN_a(a^2 - r_q^2)\rho_g}{2aq^2 D_{it}} - \Delta. \quad (5.21)$$

Equation (5.21) can be substituted into equation (5.17) to yield the transcendental equation in r_q .³⁷

$$-\frac{N_a(a^2 - r_q^2)}{2aqD_{it}} - \Delta = -\frac{qN_ar_q^2}{2\varepsilon} \left[-\frac{a^2}{2r_q^2} + \ln\left(\frac{a}{r_q}\right) + \frac{1}{2} \right] + \psi_0. \quad (5.22)$$

Equation (5.22) can be solved numerically to yield r_q . However, this equation cannot be solved for all values of a . For a defined set of N_a and D_{it} values, there exists a certain critical GaAs nanowire radius, a_{crit} , for which the nanowire is fully depleted (i.e., $r_q = 0$). To find a_{crit} , Equation (5.22) can be solved in the limit as r_q approaches 0. For $a > a_{crit}$, r_q is given by the solution to the transcendental equation (5.22). Conversely, for $a < a_{crit}$ then $r_q = 0$. With ψ_0 and r_q determined, a full expression of the potential in a partially depleted nanowire ($r_q > 0$) can be determined for a wide variety of a , N_a and D_{it} values.

Table 5.1 shows several parameters need for our next calculations, some of them calculated using equations (5.15) - (5.22).

Table 5.1. Some parameters of four investigated samples. **L** is the NW length

Sample No.	$N_a (cm^{-3})$	$F_{1/2} (\eta)$	$L (nm)$	$a (nm)$	$r_q (nm)$	$\psi_0 (V)$
1	2E17	$0.02 \pm 2.26E-5$	1067 ± 10	180 ± 4.1	$101.51 \pm 5.74E-5$	$0.612 \pm 2.93E-5$
2	1E18	$0.11 \pm 11.3E-5$	1702 ± 7	201 ± 2.7	$169.68 \pm 2.94E-5$	$0.653 \pm 3.01E-5$
3	1E19	$1.01 \pm 1.13E-5$	3373 ± 5	265 ± 2.5	$251.72 \pm 1.48E-5$	$0.707 \pm 4.01E-5$
4	5E19	$5.02 \pm 5.65E-5$	1852 ± 13	180 ± 5.6	$173.84 \pm 3.49E-5$	$0.748 \pm 5.06E-5$

5.4 Results and Discussion

For the measurements presented here, the photon energy of 650 eV for samples numbers 1 and 2, and 648.3 eV for samples numbers 3 and 4 had been performed. After scanning photo electron microscopy mapping of the samples, Ga 3d and As 3d core level emission was recorded at different positions along single nanowires. The data evaluation shows inhomogeneous distribution of Be dopants along nanowires. This also

includes sample No.3 and sample No.4, which were doped within the middle part only (green parts in Figure 5.2b and Figures 5.9 and 5.10).

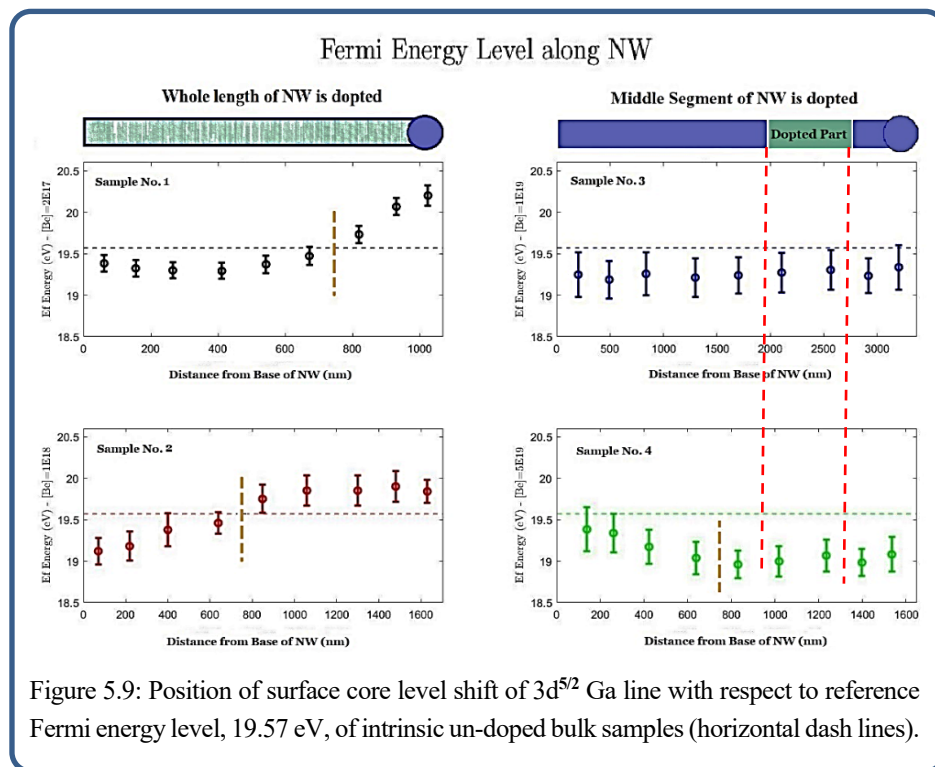
Following equation (5.6) $\psi(r)$ and subsequently E_F are a function of N_A , i.e. the local Be concentration. The evaluated surface potential ψ_s (multiplied by unit charge q) is quantitatively equal to $E_F - E_i$. The calculation includes the nanowire radius a , the surface state density D_{it} and the acceptor concentration N_A .

Using nanowire images taken by the scanning photo-electron microscopy imaging mode, information from every nine point along nanowires are available. For each segment we determined the Surface Core Level Shift (SCLS) with respect to the Ga $3d^{5/2}$ line. Table 5.2 shows the deduced Fermi energies and the Be concentration N_A . At the surface of nanowires (for $r = a$) calculated using equation (5.22). Figures 5.9 and 5.10, show corresponding graphs for values of Table 5.2, for segments 1 to 9 where segment 1 is always located at the nanowire top. In Figure 5.9 we show E_F deduced from the position of core energy level of $3d^{5/2}$ Ga line with respect to reference value of un-doped bulk samples to be of 19.57 eV. Figure 5.10 shows the respective Be concentrations.

Surprisingly also sample No.3 and sample No.4 did show an almost uniform Be distribution along the nanowires. The surface core level shift of sample No.3 is -0.149 eV which corresponds to a Be concentration $1 \times 10^{19} \text{ cm}^{-3}$ in agreement with nominal value. In contrast, sample No.4 shows an always decreasing Be concentration from the doped segment towards the top and the bottom end of the nanowire. That must be explained by the fact that the Be atoms did diffuse across the whole nanowire during growth. On the other hand, sample No.1 and sample No.2, which nominally were uniformly doped, both show a changing Be concentration which is close or higher than the nominal concentration close to the bottom but significantly lower towards the nanowire top. It probably caused by shadowing effect during growth, or maybe due to not completely cleaned impurities from nanowires surface, like oxides.

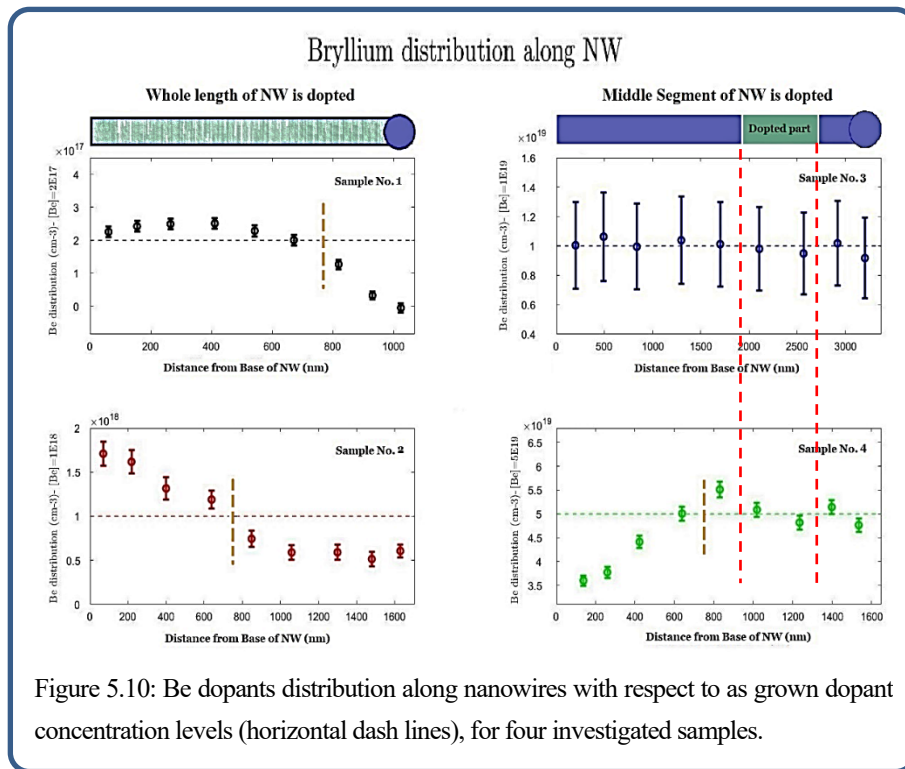
Table 5.2: Fermi Energy Level, Deviation with respect to intrinsic energy of un-doped bulk sample and measured Be dopants concentration for line profiles extracted from nine parts along nanowires. ΔE_F is error of E_F and ΔN_a is the error values of N_a

	Segment No.→	1_Top	2	3	4	5	6	7	8	9
Sample No. 1	E_F (eV)	20.202	20.068	19.733	19.473	19.373	19.293	19.30	19.324	19.384
	ΔE_F (eV)	0.249	0.204	0.204	0.214	0.214	0.191	0.196	0.196	0.196
	$E_F - E_i \equiv q\psi$ (eV)	0.632	0.498	0.163	-0.097	-0.197	-0.277	-0.27	-0.246	-0.186
	$N_a \times 10^{17} (\text{cm}^{-3})$	0.056	0.321	1.265	1.997	2.278	2.504	2.484	2.417	2.248
	$\Delta N_a \times 10^{17} (\text{cm}^{-3})$	0.139	0.122	0.142	0.163	0.169	0.161	0.163	0.162	0.158
Sample No. 2	E_F (eV)	19.84	19.9	19.85	19.851	19.75	19.46	19.377	19.18	19.12
	ΔE_F (eV)	0.28	0.367	0.367	0.36	0.336	0.26	0.395	0.35	0.32
	$E_F - E_i \equiv q\psi$ (eV)	0.27	0.33	0.28	0.281	0.18	-0.11	-0.193	-0.39	-0.45
	$N_a \times 10^{18} (\text{cm}^{-3})$	0.607	0.515	0.591	0.590	0.745	1.189	1.316	1.618	1.710
	$\Delta N_a \times 10^{18} (\text{cm}^{-3})$	0.073	0.082	0.086	0.084	0.088	0.099	0.126	0.134	0.134
Sample No. 3	E_F (eV)	19.337	19.234	19.305	19.273	19.24	19.213	19.258	19.188	19.248
	ΔE_F (eV)	0.538	0.418	0.478	0.478	0.438	0.459	0.519	0.449	0.539
	$E_F - E_i \equiv q\psi$ (eV)	-0.233	-0.336	-0.265	-0.297	-0.33	-0.357	-0.312	-0.382	-0.322
	$N_a \times 10^{19} (\text{cm}^{-3})$	0.918	1.018	0.949	0.980	1.012	1.039	0.995	1.063	1.005
	$\Delta N_a \times 10^{19} (\text{cm}^{-3})$	0.275	0.288	0.277	0.284	0.288	0.297	0.292	0.302	0.297
Sample No. 4	E_F (eV)	19.081	18.983	19.067	18.997	18.887	19.018	19.172	19.338	19.383
	ΔE_F (eV)	0.419	0.329	0.379	0.361	0.329	0.388	0.408	0.468	0.528
	$E_F - E_i \equiv q\psi$ (eV)	-0.489	-0.587	-0.503	-0.573	-0.683	-0.552	-0.398	-0.232	-0.187
	$N_a \times 10^{19} (\text{cm}^{-3})$	4.764	5.141	4.818	5.088	5.511	5.007	4.413	3.774	3.601
	$\Delta N_a \times 10^{19} (\text{cm}^{-3})$	0.139	0.15	0.143	0.145	0.16	0.147	0.131	0.114	0.106



5.5 Conclusion

We have shown that scanning photoemission spectroscopy can be successfully used to monitor the surface Fermi level and subsequently the surface acceptor concentration of single GaAs nanowires doped with Beryllium in the range from 10^{17} to 10^{19} cm⁻³. Data evaluation has been performed using the approach published by M Fanetti ²⁵, reveals that the results verify the amount of nominal doping concentration, However, in case of low doped nanowires (samples No.1 and sample No.2), which are doped over the entire nanowire length, the acceptor concentration decreases from bottom towards the top. Since the doping was performed by growing a doped GaAs layer onto the GaAs core our finding might be explained by shadowing effect of the neighbored nanowires as explained by Al- Humadi ⁴¹, or maybe by not completely cleaned impurities from nanowires surface, like oxides. On the other hand, the highly doped NWs show rather uniform doping distribution. This could be surprising considering the fact that only a middle part of the NW has been doped.



Furthermore, the results highlight the fact that the actual doping across the nanowires population on a given sample can be highly inhomogeneous, with differences observed even between neighboring nanowires. Wherever present, such differences are usually found to correspond to morphological differences in the nanowires, suggesting that the local doping strongly depends on the local growth conditions.

*T*his dissertation explores the Strain and thermal behavior of GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ core-shell semiconductor nanowires through theoretical modeling and advanced experimental techniques. Strain engineering, a key method for tailoring electronic and optical properties in semiconductors, is studied in detail to understand its role in device optimization.

A theoretical framework is developed to model axial strain in semiconductor NWs using continuum mechanics and elastic theory. Building on this, synchrotron-based X-ray diffraction techniques are employed to experimentally investigate strain relaxation phenomena in GaAs/ $\text{In}_x\text{Ga}_{1-x}\text{As}$ NW hetero-structures. A critical indium concentration is identified, above which strain relaxes plastically, leading to the formation of indium-rich surface mounds—confirmed through reciprocal space mapping and SEM imaging.

Transient thermal behavior is also investigated using femtosecond laser pump and X-ray probe techniques. This allows for the time-resolved analysis of laser-induced thermal expansion, demonstrating a direct correlation between laser power and NW expansion, with clear distinctions between zinc blende and wurtzite phases.

Finally, the axial distribution of Beryllium dopants is characterized via spatially resolved X-ray Photoelectron Spectroscopy, highlighting the

influence of growth mechanisms and geometrical effects on dopant profiles.

This work contributes a comprehensive understanding of how mechanical strain, thermal excitation, and dopant diffusion interplay in III–V nanowire systems, advancing their potential in nanoscale electronic and optoelectronic applications.

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