

NORTHWESTERN UNIVERSITY

Total Tomography of III-As Nanowire Emitters: Atom Probe Tomography and X-ray Imaging
of Nanowire Heterostructures

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

Megan O. Hill

EVANSTON, ILLINOIS

December 2020

© Copyright by Megan O. Hill 2020

All Rights Reserved

ABSTRACT

Total Tomography of III-As Nanowire Emitters: Atom Probe Tomography and X-ray Imaging of
Nanowire Heterostructures

Megan O. Hill

The three-dimensional (3D) nanoscale structure of III-As nanowires is correlated with optical and electronic property measurements to deconvolve the contributions of strain, composition, and crystal structure to characteristics of interest for future electronic and optoelectronic devices. Multiple advanced two-dimensional (2D) and 3D characterization techniques are employed such as atom probe tomography, nano-probe X-ray diffraction microscopy, Bragg coherent diffraction imaging, and Bragg X-ray ptychography.

Atom probe tomography is used to map the distribution of Si dopants in catalyst-free InAs nanowires at different *in-situ* doping conditions used during MBE growth. Doping is homogeneous in the core of the nanowires at concentrations of mid- 10^{18} cm^{-3} regardless of the dopant flux, but an excess of Si is observed near the surface of the nanowires, overlapping with a native oxide. Measurement of carrier concentrations at each nominal doping level are in agreement with the measured chemical doping levels, suggesting nearly complete dopant activation in the nanowire core.

A new approach to coherent diffraction imaging called multiangle Bragg projection ptychography is formalized and demonstrated experimentally. 3D strain and structure in InGaAs nanowires was reconstructed with better than 50 nm and 2 nm spatial resolutions respectively. Bragg coherent diffraction

imaging is performed on GaAs nanowires with embedded InGaAs quantum wells (QWs) of different thickness on each facet. 3D reconstructions of in-plane strain fields reveals the likely presence of dislocations at the thicker facets (10,20 nm) and coherent growth at the smaller facets (2,4 nm).

Correlative imaging is performed on InGaAs QWs in a GaAs nanowire which show a blue shift in emission toward the top of the nanowire via spatially resolved cathodoluminescence (CL). Directly correlated to CL, electron back-scatter diffraction reveals a polytypic structural change aligned with the shift in emission. X-ray nano-probe diffraction is used to investigate the QW strain along the nanowire length, but shows no variation. Atom probe tomography correlated with CL shows no change in QW morphology, but an increase in In content on the wurtzite portion of the QW is observed. Band structure calculations are used to determine the effect that each structural change has on the emission shift, revealing that composition and polytype structure both play an important role.

Acknowledgments

I have so many thanks to give. To my advisor Lincoln Lauhon, thank you for the guidance and countless hours of mentorship you have given me over the years. You have provided me with more resources than I could have imagined coming into a PhD. Thank you for your understanding, for the freedom you have provided me, and for your strong dedication to education. Thank you to my committee members, Stephan Hruszkewycz, Michael Bedzyk, and Peter Voorhees, for your helpful discussions and guidance. In particular to Stephan, my unofficial second advisor, your mentorship and encouragement has meant the world to me. I never knew I could learn so much from one person. Thank you for always believing in me.

This thesis would not be possible without the hard work and collaboration of many researchers: Gregor Koblmüller, Thomas Stettner, Jonathan Becker, Julian Treu, Max Sonner, and Paul Schmiedeke at TU Munich; Lutz Geelhaar and Jonas Laehnemann at Paul-Drude-Institut; Stephan Hruszkewycz, Irene Calvo-Almazan, Siddharth Maddali, Martin Holt, Andrew Ulvestad, Brian Stephenson and Wonsuk Cha at Argonne National Lab; Yong Chu, Xiaojing Huang, Hanfei Yan, and Evgeny Nazaretski at Brookhaven National Lab; Virginie Chamard and Marc Allain at CNRS; and Ullrich Pietsch, Arman Davtyan, and Ali Al Hassan at U. Siegen. Special thanks to Jesper Wallentin and Susanna Hammarberg. These professors, scientists, postdocs, and students have been amazing to work with and inspire me to continue to be a better scientist. This work was supported in part by the National Science Foundation via grants DMR-1611341 and DMR-1905768. This work was also supported by an NSF GRFP.

Thanks to the many amazing mentors I have had over the last eight years of research: Nari Jeon, Victoria Sorg, Suki Zhang, Xuetian Ma, Byungki Jung, and especially Michael Thompson. To my colleagues and friends in the Lauhon group, thank you for your support and kindness over the years and for always helping me with beamtime. Thank you to Chunyi Huang, for consistently bringing kindness

and joy to the work we do. To Michael Moody, thank you for being an endless source of both scientific inspiration and compassion. Thanks to all those researchers at Northwestern who made this work possible including Dieter Isheim, Karl Hagglund, Benjamin Myers, Tirzah Abbott, and Jonathan Emery.

Thanks to the friends and colleagues who have made my PhD experience so enjoyable. To Tom, our summer of research together was one of the most enjoyable times in my PhD. You have taught me so much and your friendship means so much to me. Thanks to my ptychography sisters, Irene and Sanna, whom I adore. I have had so much fun with you two, from writing reconstruction scripts together to scouring synchrotrons for souvenir mugs or the best late night espresso. To my many friends at Northwestern, but especially to Allie, Jen, and Tad. Tad, you have kept me laughing through many tough times. Jen, becoming your roommate was the best choice I made in grad school. Allie, you have been a source of unending love and compassion. You three are my dearest family and I could not have done this without you. Thank you to my mom, dad, Nicole, Erin, and Becca, you all have always supported me, even if you think I'm a nerd. Mom and dad, thank you for supporting my dreams and always convincing me things will work out for the better. To Etta and Sloane, thank you for the smiles and hugs needed to get me through these last few years. I am beyond grateful to my partner Erik. You have supported me, encouraged me, and loved me even when it was hard. I love you very much and cannot wait to finally live on the same continent. Finally, thanks to the Lord 'for from Him and through Him and to Him are all things', Romans 11:36a.

Table of Contents

ABSTRACT	3
Acknowledgments	5
Table of Contents	7
List of Figures	9
List of Abbreviations	12
Chapter 1. III-As Nanowire Emitters: Applications, Growth, and Challenges	15
1.1. Introduction to III-As Nanowires	15
1.2. Semiconductor Nanowire Growth	17
1.3. III-As Nanowires as Compact Near-IR Emitters	20
1.4. Structural Features of Ternary III-As Nanowires	22
Chapter 2. Tools for Single-Nanowire Total Tomography	32
2.1. Why is Correlative Tomographic Imaging Required?	32
2.2. Atom Probe Tomography for 3D Composition Mapping	34
2.3. Electron Microscopy for Probing Structure, Composition, and Strain	43
2.4. Characterization of Strain and Structure using Synchrotron X-rays	50
2.5. Simulating Strain and Diffraction in Nanowires Heterostructures	80
2.6. Electrical and Optical Characterization of Nanowires	92
Chapter 3. Composition and Dopant Mapping in InAs Nanowires	95
3.1. Motivation of Research	95

3.2. Introduction	95
3.3. Results and Discussion	97
3.4. Summary	110
Chapter 4. 3D Ptychography for Strain Mapping in Extended Objects	112
4.1. Motivation for Research	112
4.2. Introduction to maBPP	114
4.3. maBPP Algorithm Description	126
4.4. Limitations and Challenges of maBPP	127
Chapter 5. Correlative Tomography of InGaAs QWs in Nanowires	130
5.1. Emission Shift in Wurzite/Zincblende InGaAs Quantum Well Heterostructures	131
5.2. Bragg Coherent Diffraction Imaging of InGaAs Quantum Wells of Asymmetric Thickness	147
Chapter 6. Outlook: Total Tomography for Characterizing Semiconductor Nanostructures	166
Bibliography	169
Appendix A. Nanowire Manipulation and Isolation for Atom Probe and Synchrotron Studies	197
Appendix B. Measuring Accurate Dopant Concentrations via Atom Probe Tomography	203
B.1. Measuring Dilute Si Dopants in InAs Nanowires	203
B.2. Variable Laser Energy Studies	205
Appendix C. Effects of Beam Defocus on Nanodiffraction Analysis	208
Appendix D. Misfit Dislocations in Asymmetric Quantum Well Nanowires	211

List of Figures

1.1	III-As emission energy as a function of composition	16
1.2	Schematic of VLS vs VS growth of nanowires	18
1.3	Sketch of different quantum structure types	20
1.4	Schematic of radial quantum well structure	21
1.5	Cross-sectional STEM showing Al segregation in GaAs/AlGaAs nanowire	23
1.6	Crystal structure of ZB vs WZ III-V	25
1.7	STEM of WZ/ZB polytypism in GaAs Nanowire	26
1.8	Schematic of nanowire facet directions with cubic and hexagonal miller notation	28
1.9	III-As lattice parameter as a function of composition	29
2.1	Schematic of local electrode atom probe tomography	35
2.2	Example of APT reconstruction and mass spectra	38
2.3	Overview of FIB lift-out procedure	41
2.4	Schematic Fresnel zone plate and multilayer Laue lens	58
2.5	Phase retrieval process for BCDI	62
2.6	Schematic of Bragg coherent diffraction imaging experiment	63
2.7	Example of BCDI reconstruction post-processing requirements	65
2.8	Phase retrieval process for Bragg ptychography	69
2.9	Description of how 3D information is encoded in 2D diffraction patterns	72
2.10	Phase retrieval process for Bragg projection ptychography	74

2.11	Example of scanning X-ray diffraction microscopy	78
2.12	Model of strain in core-multishell nanowire by FEM in COMSOL	82
2.13	Example FEM simulations of nanowire QWs using nominal strain and APT as input	85
2.14	Comparison of critical thicknesses for InGaAs/GaAs films vs. core-shell nanowires	86
2.15	Example scattering geometry for kinematic scattering simulations	89
2.16	Example simulated diffraction patterns using kinematic scattering	90
3.1	SEM of undoped and Si-doped InAs nanowires	98
3.2	Seebeck effect measurements of Si-doped InAs nanowires	101
3.3	4-terminal NW-FET of Si-doped InAs nanowires	103
3.4	APT mass spectrum for Si-doped InAs nanowires	106
3.5	APT reconstruction of a Si-doped InAs nanowire	108
3.6	Concentrations of bulk Si dopants (APT) and n-type charge carriers in InAs nanowires	109
4.1	Experimental setup of HXN Beamline for maBPP measurements of nanowires	116
4.2	Example diffraction patterns and description of nanowire twisting in maBPP experiment	119
4.3	maBPP reconstruction of $2\bar{1}\bar{1}0$ strain in InGaAs nanowire	121
4.4	maBPP reconstruction of $01\bar{1}0$ peak showing defects in InGaAs nanowire	123
5.1	SEM, CL, and EBSD of (In,Ga)As core-shell nanowire	133
5.2	NanoXRD of (In,Ga)As core-shell nanowire	135
5.3	APT and correlated CL of (In,Ga)As core-shell nanowire	138
5.4	Strain and transition energy simulations for WZ-ZB (In,Ga)As core-shell nanowire	140
5.5	Growth schematic and SEM of asymmetric InGaAs QW nanowires	149

5.6	Outline of available peaks for ZB nanowire BCDI and schematic of a BCDI measurement	153
5.7	Example BCDI diffraction patterns and reconstructions for asymmetric QW nanowires	155
5.8	Experimental and simulated BCDI reconstructions for asymmetric QW heterostructures	158
5.9	Line cuts from BCDI strain reconstruction across QWs	160
5.10	Experimental and simulated phase maps of BCDI reconstructions for asymmetric QWs and mapping of dislocation cores in 3D.	163
A.1	Pick-up of nanowires for APT	198
A.2	Direct pick-and-place of nanowires for correlative APT	199
A.3	Overview of nanowire transfer to Si diving-boards for synchrotron measurements	201
B.1	Change in mass spectra noise by modifying laser pulse frequency	204
B.2	Variations in APT concentration with laser pulse energy in an InAs nanowire	206
B.3	Change in APT field of view with laser energy	207
C.1	Simulated effect of beam defocus on nanodiffraction	208
C.2	Experimental measurement of effect of beam defocus on nanodiffraction	210
D.1	Comparison of experimental phase maps of asymmetric QW nanowire with simulated defect structure	211

List of Abbreviations

NW - nanowire

InGaAs - $\text{In}_x\text{Ga}_{x-1}\text{As}$

AlGaAs - $\text{Al}_x\text{Ga}_{x-1}\text{As}$

III-V - group-III and group-V compounds

LED - light-emitting diodes

III-As - group-III and arsenic compounds

IR - infrared

UHV - ultra high vacuum

MBE - molecular beam epitaxy

VLS - vapor-liquid-solid

VS - vapor-solid

SAE - selective area epitaxy

FET - field effect transistor

1D - one dimensional

2D - two dimensional

3D - three dimensional

QW - quantum well

QD - quantum dots

SQW - single quantum well

MQW - multi quantum well

STEM - scanning transmission electron microscopy

HAADF - high angle annular dark field

WZ - wurtzite

ZB - zincblende

SF - stacking fault

c-s - core-shell

EDS - energy dispersive spectroscopy

APT - atom probe tomography

LA-APT - laser assisted atom probe tomography

LEAP - local electrode atom probe

ToF - time of flight

m/n - mass-to-charge ratio

LA-APT - laser assisted atom probe tomography

SEM - scanning electron microscopy

FIB - focused ion beam

EBSD - electron back-scattered diffraction

TEM - transmission electron microscopy

HRTEM - high resolution transmission electron microscopy

SAED - selected area electron diffraction

DF - dark field

BF - bright field

ADF - annular dark field

DFEH - dark field electron holography

GPA - geometric phase analysis

NBED - nano-beam electron diffraction

N-PED - nano-beam precession electron diffraction

EELS - electron energy loss spectroscopy

FWHM - full width half maximum

FEL - free electron laser

BW - bandwidth

LINAC - linear accelerator

DLSR - diffraction limited storage ring

CRL - compound refractive lens

KB - Kirkpatrick-Baez mirror

ZP - zone plate

MLL - multilayer Laue lens

CDI - coherent diffraction imaging

BCDI - Bragg coherent diffraction imaging

FFT - fast Fourier transform

CCD - charge coupled device

RSM - reciprocal space map

BP - Bragg ptychography

PIE - Ptychographic Iterative Engine

3D-BP - three dimensional Bragg ptychography

3DBPP - three dimensional Bragg projection ptychography

maBPP - multiangle Bragg projection ptychography

SXDM - scanning X-ray diffraction microscopy

DS - Debye-Scherrer

FEM - finite element modeling/method

NW-FET - nanowire-field effect transistor

PL - photoluminescence

CL - cathodoluminescence

CHAPTER 1

III-As Nanowire Emitters: Applications, Growth, and Challenges**1.1. Introduction to III-As Nanowires**

Silicon (Si) remains the most cost effective and robust platform for microelectronics and photonics. As such, considerable effort has been made to integrate direct band-gap, high-efficiency photonic semiconductors, such as III-Vs, onto Si. This would allow for low cost, high performance solar cells and light-emitting diodes (LEDs). Additionally, the ability to couple photonic components with traditional Si logic opens doors to new types of low-power computing [1, 2]. In particular, narrow-bandgap III-Arsenides (III-As), which include GaAs, AlAs, InAs, and their ternary/quaternary compounds, are of interest for optical applications in the visible and near-infrared (near-IR). As depicted in 1.1, ternary compounds of III-As materials allow for tunable emission energy, with a linear relationship between composition and energy according to Vegard's Law [3]. In addition to having a direct bandgap, the ability to tune the bandgap using composition in III-As makes it clearly advantageous for Si photonics.

As an example, GaAs has been used in photovoltaics for decades as it has been shown to significantly outperform Si in terms of conversion efficiency [6]. However the five-fold higher cost of GaAs as compared to Si limited its use, for much of its history, to space craft and satellite power systems where there is a greater need for robustness to radiation damage [7]. Efforts have been made to integrate GaAs onto Si in order to reduce the amount of material necessary and in turn reduce the cost, but until recently, the efficiency of GaAs on Si solar cells suffered due to defect formation at the GaAs-Si interface. Herein lies the main challenge of producing low-cost, high performance III-As photonics. The high lattice mismatch between Si (lattice constant of 5.43 Å) and III-As materials (lattice constant between 5.65 and 6.05 Å) results in threading dislocations and phase-domain boundaries that degrade the III-As layer [8, 9, 10, 11].

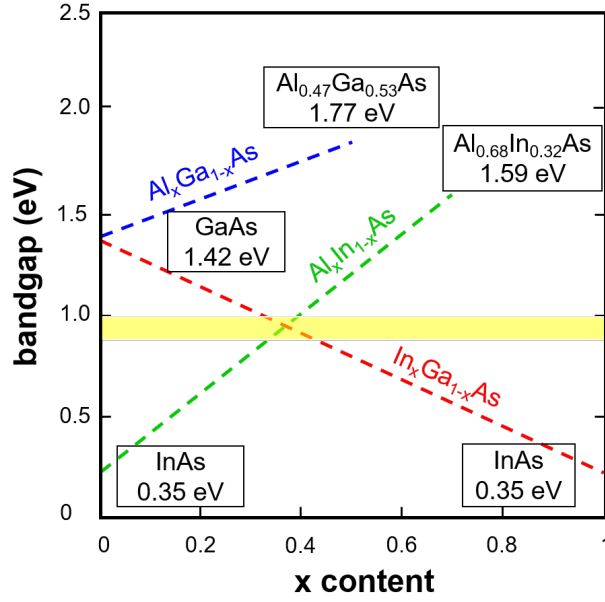


Figure 1.1. Emission energy (eV) as a function of composition (x content) for ternary compounds of GaAs, InAs, and AlAs. Emission ranges from visible to mid-IR [3]. Al containing compounds have cutoffs at higher Al content due to transitions to in-direct bandgap [4]. A yellow band is shown in the telecommunication regime (1260-1625 nm) [5]

Methods for integrating III-As thin films onto Si while minimizing defects have been developed, such as engineering strain-layer superlattice buffers between the Si and the desired III-As film to mitigate the mismatch or by using wafer-bonding techniques [12, 13]. However, the buffer layer approach, while significantly lowering defect densities, falls short in creating high enough quality films for most applications. Wafer-bonding can be effective in removing defects from the Si-III-As interface, but this technique suffers from high processing costs compared to epitaxial growth methods [14, 15, 16]. In 2004, Mårtensson et al. [17] first demonstrated the ability to epitaxially grow III-V nanowires (InP and GaAs) on Si, which due to the small wire diameter allowed for strain accommodation and defect-free relaxation at the Si III-V interface. Since then, extensive studies of III-V nanowire growth on Si have been reported including growth of numerous types of III-V nanowires, various growth methods, and on selective-area growth techniques [18, 19, 20, 21, 22]. In addition to the ability to grow nanowires epitaxially on Si, they offer a number of advantages over traditional thin films. The small amount of III-As material used in

the nanostructures means a greater reduction in materials costs. The vertical 3D nanowire geometry is ideal for light trapping applications, such as solar cell arrays or single nanowire lasers [23]. Additionally, the nanowire geometry allows for the growth of unique heterostructures that accommodate large strains without defect formation; additional discussion is provided in Section 1.2.2. Of course, achieving high performance III-As nanowire devices does not come without challenges, as III-As nanowire heterostructures can exhibit complex variations in composition, strain, crystal structure, and morphology as discussed in Section 1.4.

1.2. Semiconductor Nanowire Growth

1.2.1. Nanowire Growth via Molecular Beam Epitaxy

The nanostructures discussed in this thesis are grown by solid source molecular beam epitaxy (MBE). MBE is a deposition technique performed in ultra high vacuum (UHV) that utilizes thermally generated beams of atomic species to grow thin films or nanostructures with atomic precision [24]. There are two main nanowire growth mechanisms in MBE growth, both named after the mass transport pathway: vapor-liquid-solid (VLS) and vapor-solid (VS) growth. Much of the initial growth studies of III-As nanowires used an impurity-mediated VLS mechanism, in which a liquid catalyst droplet of foreign metal (Au,Ag) is deposited on a substrate and used to promote vertical growth [25, 26, 27]. For example, for GaAs nanowire growth, the metal particle absorbs vapor phase precursors including Ga and As, until it is supersaturated, at which point solid phase GaAs is crystallized at the base of the droplet. The droplet continues upward, crystallizing GaAs below until the conditions are changed such that the droplet is consumed or solidifies. This mechanism is shown in Figure 1.2(a). Though the use of a foreign metal catalyst allows for a high level of control over nanowire growth, it can result in the incorporation of impurities throughout the nanowire, which can greatly degrade electronic or optical performance. For example, Au or Ag impurities are well known to form deep-level trap in Si [28]. Thus, more recent efforts have been made to grow nanowires controllably without the use of foreign catalytic materials, for instance Ga liquid droplets have been used to grow GaAs nanowires [29, 30].

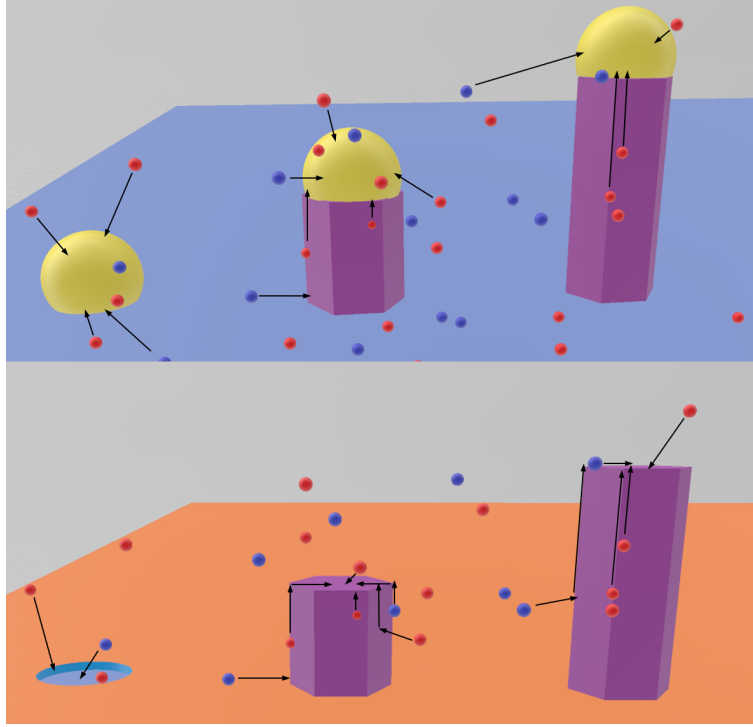


Figure 1.2. Schematic of VLS (top) and VS (bottom) growth processes of nanowires. Schematic shows the liquid catalyst droplet (yellow), nanowires (purple), Si substrate (blue), and SiO₂ (orange). Growth process is demonstrated from left to right.

While self-catalyzed growth is useful in numerous device applications, this growth has been shown to cause segregation of dopant species and prevent the formation of atomically sharp vertical interfaces [31, 32]. An alternative is to grow nanowires completely catalyst-free, using VS growth, where nanowires are either randomly nucleated or nucleated in open holes of a oxide template, known as selective area epitaxy (SAE) [33, 34, 35]. In this mechanism, precursor species are deposited on the substrate and diffuse to nucleation sites. These mobile surface adatoms diffuse to the VS interface of the nanowire, and are incorporated on preferred growth facets, which dictate the vertical growth. Vertical growth continues until the supply of precursor atoms is used up or until the species diffusion length prevents atoms from reaching the top nanowire VS interface. This mechanism is shown in Figure 1.2(b).

Controlling nanowire growth in MBE primarily involves tuning the substrate temperature and the flux of atomic species (via heating of effusion cells). The ratio of group III and group V species flux plays

a large role in determining the nanowire size and crystal structure. Additionally, substrate preparation plays a large role in nanowire nucleation. VLS nanowires require the deposition or random nucleation of liquid catalyst droplets before or during MBE growth. For VS nanowire growth, typically an SiO_2 film is grown on the Si substrate, and pinhole openings are randomly nucleated or electron-beam patterned such that growth can only occur in these openings (see Ref. 36 for details). Utilizing the high precision of MBE, complex nanowire heterostructures can be grown as discussed in the next section (1.2.2).

1.2.2. Nanowires allow for unique heterostructures

Nanowires with sufficiently small diameters to exhibit electron and/or photon confinement are of interest for applications including field-effect transistors (FETs) [37, 38, 39] and LEDs and compact lasers [40, 41, 42]. More recently, semiconducting quantum wires, proximity-coupled with an s-wave superconductor, have been proposed as hosts for Majorana Fermions for topological quantum computing [43]. Most nanowires are too large (diameter >100 nm) to observe quantum effects. However, the structure or composition of the nanowire can be modified to create other electronically confined structures within the nanowire. By using the nanowire as a support for other quantum structures, the range of applications is broadly expanded. Figure 1.3 demonstrates the types of electronically confined structures that can be embedded in nanowires, including quantum wells (confined in 1D), quantum wires (2D), and quantum dots (3D).

Axial heterojunctions can be formed in nanowires by modifying the flux of different atomic species partway through the growth process. This can be done under VLS or VS growth mechanisms. For radial junctions, or core-shell nanowires, the core can be grown by either VLS or VS mechanisms. However, following the growth of the nanowire core, shells are deposited through VS growth only. Quantum wires and quantum dots can also be grown on or inside nanowires, and have even been observed to form unintentionally due to alloy fluctuations in III-Vs [45, 46]. A detailed review of the growth of quantum structures using MBE can be found in Reference 44.

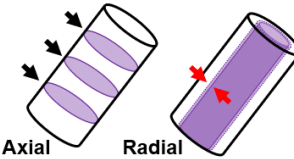
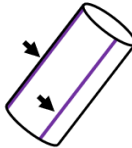
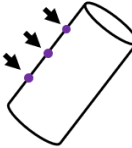
Confined dimensions	Quantum structures	Sketch
1D	Quantum Wells (QWs)	 The sketches for Quantum Wells (QWs) show two cylindrical structures. The first, labeled 'Axial', has three horizontal purple ellipses inside a cylinder, with two black arrows pointing along the cylinder's length. The second, labeled 'Radial', has a solid purple cylinder with two red arrows pointing radially inward from the outer surface.
2D	Quantum Wires	 The sketch for Quantum Wires shows a cylinder with a single vertical purple line inside, and two black arrows pointing along the cylinder's length.
3D	Quantum Dots (QDs)	 The sketch for Quantum Dots (QDs) shows a cylinder containing three small purple dots. Two black arrows point along the cylinder's length, and two additional black arrows point radially inward from the cylinder's surface towards the dots.

Figure 1.3. Sketch summary of the different quantum structure types attending to the number of confined dimensions. Adapted from Reference 44 by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

1.3. III-As Nanowires as Compact Near-IR Emitters

For the last half-century, improvements in Si-based electronics have relied primarily on the shrinking of transistors logic components. However, as transistors reach the sub-10 nm range a fundamental shift is needed in materials or device architecture in order to continue advances in computing and communications. Many routes are being actively researched, including spintronics, quantum computing, and optical computing. However, as these paradigm shifts are explored, routes to improving traditional transistor technology are also being addressed, such as increasing the speed and reducing the power used during communication between individual logic components. For example, just as fiber optics provides a faster, more energy efficient, and more robust way communicate over long distances, optical interconnects would do the same at the microscale. In this scheme, compact emitters and detectors would be connected using patterned Si waveguides. Laser pulses between the emitter/detector would be used to transfer information within the transistor chip. This would act as a much faster mode of communication and would generate significantly less loss as compared to electrons moving through copper interconnects.

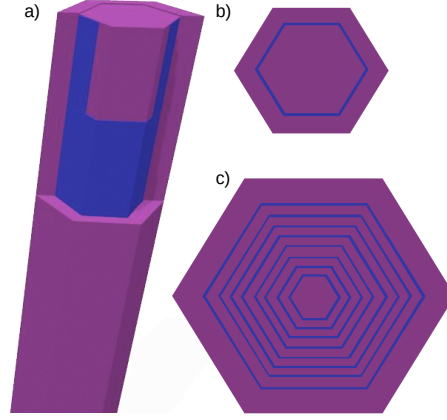


Figure 1.4. Schematic of radial quantum well structure. a) 3D view of InGaAs QW embedded in (Al,Ga)As. b) Cross-section of core-shell QW structures. c) Cross-section of multi-well QW structure, useful in lasing applications. (Al,Ga)As is purple and InGaAs is blue.

GaAs nanowires with embedded radial quantum wells (QWs) of (In,Ga)As are of interest as these compact emitters and detectors. Since these nanowires can be grown directly on Si and can be tuned to emit in the Si-transparent near infrared regime (IR), such that there are minimal absorption losses within the Si waveguides. GaAs-based nanowires have shown to act as a good gain medium and optical Fabry-Pérot cavity for low-threshold lasing [23]. Additionally, Stettner et.al, have grown GaAs nanowires directly onto Si waveguides and demonstrated their ability to couple light into the waveguide [47]. Though GaAs nanowires are good candidates for lasing and monolithic growth, their near-IR emission, above the Si absorption edge, results in significant loss during transport through the waveguide. The growth of InGaAs radial QWs has been proposed as a solution to increase the emission wavelength of these GaAs-based nanowire lasers into the Si-transparent IR regime [48, 49, 50]. In this heterostructure, the QW would act as the active gain medium, transferring light to the GaAs core which acts as an optical cavity to enhance emission.

Figure 1.4 shows a schematic of a single quantum well (SQW) (a,b) and multi quantum well (MQW) structures where InGaAs (blue), confined to <10 nm, would act as the active material. The increased In content increases the emission wavelength. Additionally, quantum wells have been shown to provide a

lower lasing threshold and improve gain as compared to their bulk counterparts [51, 52]. These types of heterostructures, primarily the SQW nanowire, are explored in this thesis.

1.4. Structural Features of Ternary III-As Nanowires

This section will discuss the numerous nanoscale inhomogeneities that may occur within III-As nanowires, and therefore what type of characterization is necessary to understand their structure-property relations. “Structure” or “structural” will be used in this work to refer to morphology, composition, strain, or crystal structure in a given nanowire sample. For clarity, crystal structure will always be referred to specifically as “crystal structure”, “polytypism” or “crystal phase”.

1.4.1. Composition and morphological fluctuations in III-As nanowires

III-As nanowire heterostructures offer a high degree of tunability in terms of emission and electronic behavior, but this comes at the cost of a high number of structural degrees of freedom which include: composition, crystal structure, strain, doping, and morphological variations. Specifically, these nanowires can present unintentional variations in composition.

The spatial distribution of group-III species within a ternary or quarternary III-As nanowire should be that of a random alloy. However, fluctuations away from a random alloy distribution have been observed in III-V nanowires. These fluctuations can act as electron scattering sites, degrading carrier mobility, and can modify the bandgap and lead to band bending [53, 54]. Researchers have been able to suppress alloy fluctuations in GaAs/AlGaAs core/shell nanowires by lowering the shell growth temperature [55]. This same behavior has been observed in epitaxial films and bulk crystals of InGaAs [56, 57].

In addition to random alloy fluctuations, larger scale composition segregation has been observed in III-As heterostructures as a result of the differences between adatom diffusion rates at different growth facets. The most common example of this comes from growth of AlGaAs shells on GaAs, where the interplay between growth kinetics and thermodynamics creates results in Al-rich bands formed along the $\langle 112 \rangle$ growth direction in the AlGaAs shell, as seen in Figure 1.5. In this case, Rudolph, et al. [58] found $[112]$ facets enriched with Al via cross-sectional high angle annular dark field scanning transmission

electron microscopy (HAADF-STEM). For a AlGaAs shell with Al concentration of 30%, enrichment up to 62% Al was found along the $\langle 112 \rangle$ directions. The Al-rich stripes arise due to an interplay between surface diffusion rate differences for Ga and Al, differences in chemical potential between the $\{112\}$ and $\{110\}$ facets, and differences in sticking coefficients of deposited atoms on these two facet families [59, 46]. Further, 3-fold symmetric variations in Al content has been observed in these wires due to polarity differences between the $\{112\}$ A and $\{112\}$ B facets. [60]

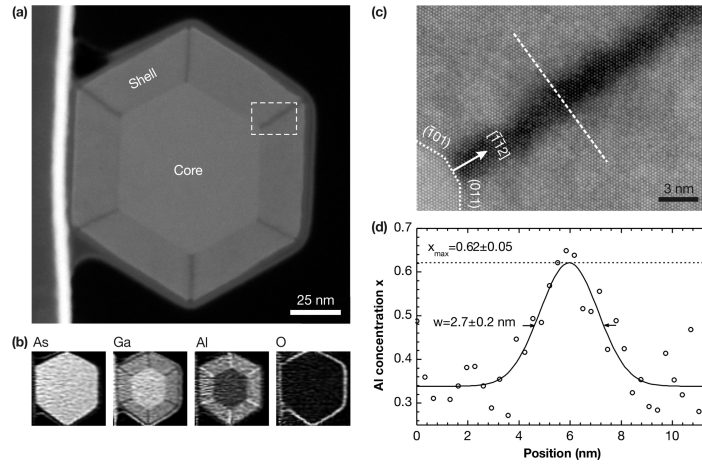


Figure 1.5. Cross-sectional STEM-HAADF showing Al segregation in GaAs/Al_{0.3}Ga_{0.7}As core/shell nanowire. (b) Elemental EDS maps of the cross-section, revealing Al segregation to the $\{112\}$ facets. (d) Detailed line map of the Al concentration taken from the line in (c). Reprinted with permission from Rudolph, Daniel, et al. Nano letters 13.4 (2013): 1522-1527. Copyright © 2013 American Chemical Society. [61]

It is critical to understand and control composition fluctuations because non-uniform composition complicates interpretation of nanowire properties, as the bandgap cannot be perfectly described by Vegard's law. Ultimately, not all composition variations (like Al enrichment in the on the $\{112\}$ facets), is possible to eliminate, but including this in our understanding of these heterostructures is necessary.

1.4.2. Doping of III-As nanowires

Though this thesis does not focus on doping in III-As nanowires, it is an important topic. Doping is required for all nanowire devices in order to create any kind of nanowire junction or to create a good

contact with metals for electrical injection (as will be needed in the case of compact emitters). As such, chapter 3 will address some challenges in doping InAs nanowires grown via the VS mechanism.

Bulk III-As materials are typically doped with group-II materials like Mg and Be for p-type doping (Mg and Be fill Ga, In, or Al sites, acting as an acceptor) [62]. Less commonly, III-As is doped with group-VI elements which act as donors when occupying As sites. Other common dopants are group-IV elements such as Si, C, and Sn. However, these group-IV elements can act as either donors or acceptors due to the amphoteric nature of III-V semiconductors [63, 64]. This means that group-IV elements can sit on either the group-III or group-V site, allowing for either n-type or p-type doping respectively. Whether group-IV elements act as donors or acceptors depends on the III-V material, the group-IV dopant element, the orientation of the growth substrate, and the growth condition [65, 66, 62]. In some cases, group-IV dopants can fill both group-III and group-V sites, resulting in compensation, this is particularly present using Ge doping, making Ge dopants generally ineffective in III-Vs [62, 67].

In addition to the complex doping nature of bulk III-Vs, III-V nanowires present additional challenges. In particular, the dopant incorporation is facet dependent. A general review of doping in nanowires is presented in Reference 68, which details how doping can greatly influence the growth rates of different facets and can lead to changes in the nanowire crystal structure. In VLS grown nanowires, dopant incorporation can happen through the liquid droplet and through vapor-solid growth on the side facets. Dopants can also diffuse into the 'bulk' during high temperature growth, further complicating the understanding of their incorporation. Even limited to droplet incorporation, the spatial distribution of dopants can be non-uniform, as seen in Ge VLS grown nanowires, where dopant concentrations are higher near the nanowire side facets due to increased dopant incorporation into lower-mobility truncated facets at the corners of the liquid droplet [69]. Numerous studies have shown similar non-uniform dopant distributions in III-V nanowires [70, 71, 72, 32, 73]. Controlling dopant incorporation requires a detailed understanding of the growth mechanisms at play during MBE growth, including the evolution of the growth front and the incorporation rates on different facets. Chapter 3 gives one example of how we can better understand dopant incorporation and the resulting electrical properties using correlated characterization and device measurement techniques.

1.4.3. Polytype crystal structure and defects in III-As nanowires

The equilibrium phase of solid-state III-As is the cubic zinc-blende (ZB) structure (space group $F\bar{4}3m$) whose structure and properties are well established. However, it has been found that in the nanowire geometry, III-As materials can form other metastable crystal phases, with the primary alternative to ZB being the hexagonal wurtzite (WZ) structure (space group $P6_3mc$) [74, 75].

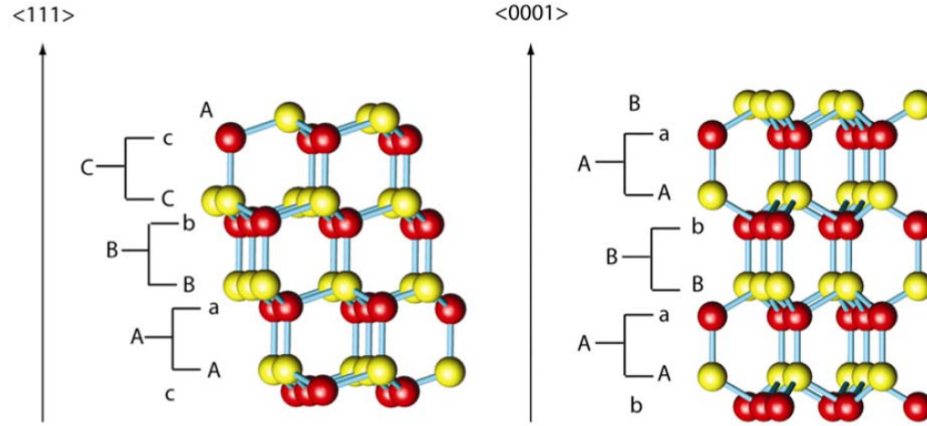


Figure 1.6. Crystal structure of ZB (left) and WZ (right) III-V. ZB shows as ABC type stacking along the $\langle 111 \rangle$ while WZ shows as ABAB type stacking along the equivalent $\langle 0001 \rangle$. Group-III represented by red atoms, group-V by yellow. Reprinted with permission from Caroff, Philippe, et al. “Crystal Phases in III-V Nanowires: From Random Toward Engineered Polytypism” IEEE J. of Selected Topics in Quantum Electronics 17.4 (2011): 830. Copyright © 2011 IEEE. [76]

For a brief introduction to this polytype system, a schematic of the stacking in III-As WZ and ZB crystals is shown in Figure 1.6. Nanowires of the ZB structure grow primarily along the $\langle 111 \rangle$ direction and of WZ structure grow along the equivalent hexagonal direction $\langle 0001 \rangle$. In this axis ZB presents an ABCABC type stacking, where each letter represents a stacking site for a single bilayer consisting of a group-III and group-V layer. Since the difference between ZB and WZ is simply a change in stacking order, it frequently occurs that WZ and ZB both appear in a single nanowire. This is demonstrated in Figure 1.7. Here a high resolution STEM image of a single GaAs nanowire projected along the $\langle 1\bar{1}0 \rangle$ direction is shown. In a magnified section (red box) the stacking order is mapped out with lines across the planes of atoms. The stacking along the $\langle 111 \rangle$ direction (from bottom to top) transitions from WZ

(ABAB) to ZB (ABC) to twinned-ZB (CBA). The ZB and twinned-ZB segments are connected with a single stacking fault (ABCACBA). Stacking faults (SF) describe planar defects that alter the periodic sequence of the crystal layers, here the **A** insertion disrupts the ZB sequence. This switching between ZB and WZ, as well as presence of SFs is common in III-As nanowires [77, 78].

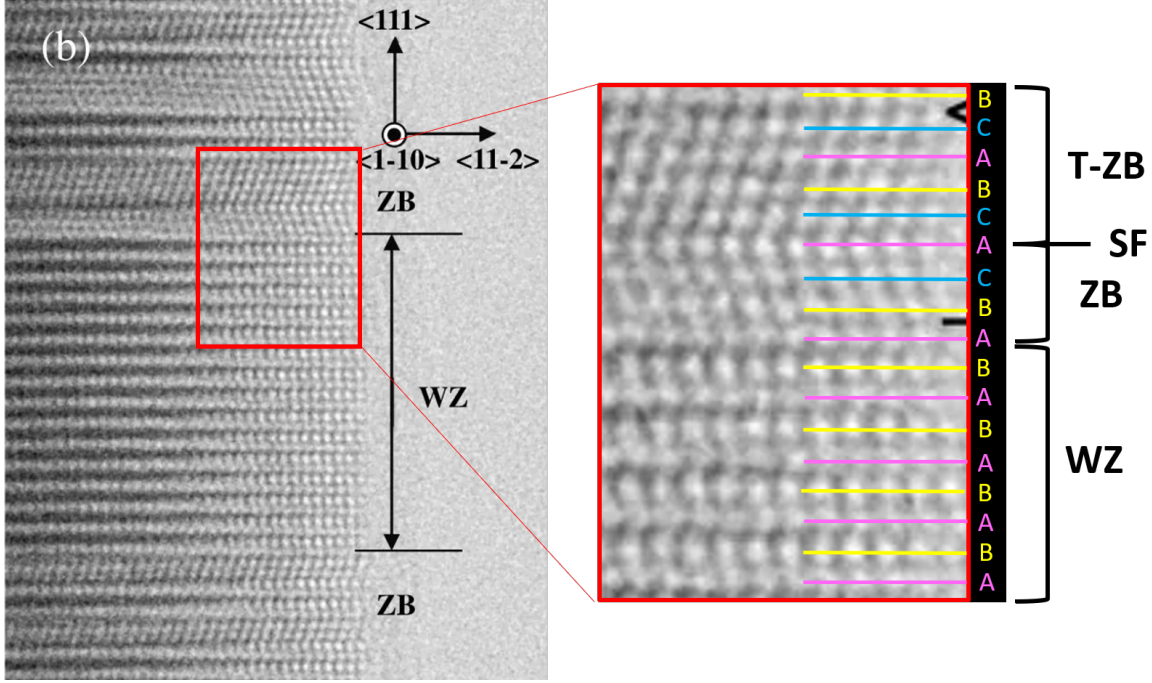


Figure 1.7. STEM image of GaAs nanowire. Nanowire switches from WZ crystal with ABAB stacking (pink and yellow lines), to ZB crystal with ABC stacking (pink, yellow, blue lines). A stacking fault (denoted SF) is present in the ZB segment, whose visible stacking sequence is ABCACBA. Adapted with permission from Yamaguchi, M., et al. “Probability of twin formation on self-catalyzed GaAs nanowires on Si substrate.” *Nanoscale Res Lett* 7 (2012):558. Copyright © 2012 Springer Nature. [79]

It wasn't until the late 2000s that this polytypism in III-As nanowires was understood well enough to control which crystal phase was grown [80, 76]. Glas et al.,[81] presented a detailed model for why this polytypism exists in III-As nanowires. Briefly, the bulk cohesive energy of ZB in III-As is lower than WZ, thus ZB is energetically favorable in bulk. There is a critical diameter at which the lower surface energy of WZ dominates over the lower bulk cohesive energy of ZB, thus forming a WZ structure. However, this does not fully explain the presence of WZ in larger nanowires, as this critical diameter

is 5.6 nm (for GaAs), and WZ is observed in much thicker nanowires than this. Glas et al. proposes that the crystal structure is dependent on whether nucleation occurs at the vapor-liquid-solid interface or the solid-liquid interface (inside the droplet or on the edge of the droplet), with the former favoring ZB growth. Formation of WZ requires that nucleation occurs at the vapor-liquid-solid interface and also requires that a high enough droplet supersaturation is present, meaning WZ formation is highly dependent on V/III flux during MBE growth. It is possible, using self-catalyzed VLS method, to grow defect-free pure WZ and ZB nanowires [82, 83, 84], to controllably switch between WZ and ZB, or add intentional twins in ZB nanowires [85, 86]. However, most nanowire structures still include numerous random SFs or polytype insertions, so these must be considered when investigating nanowire properties.

The electronic behavior of WZ in III-As has been widely debated even in the last decade. Since III-As does not form WZ in the bulk, obtaining band structure parameters has been a non-trivial pursuit. However, it is now commonly accepted that in binary III-As nanowires, WZ has a larger bandgap than ZB (only 5-20 meV larger for GaAs, ~ 60 meV for InAs) [87, 88, 89, 90], and heterojunctions of WZ and ZB form a type-II band alignment with a 30-100 meV offset depending on the group-III species [91, 92, 93]. The difference in band structure between these two polytypes creates unique opportunities for forming crystal phase quantum disks in III-As nanowires by controlling the crystal phase along the nanowire growth axis. These WZ/ZB quantum disks have been proposed as potential single photon emitters, because it is difficult to create the same atomically sharp interface using a change in composition [94, 93, 95]. Though this polytypism is a potentially useful feature in III-As nanowires, if crystal switching is not properly considered, SFs and WZ/ZB insertions can act as scattering centers, degrading the optical and electronic properties [80].

Since this thesis will investigate both WZ, ZB, and mixed phase nanowires, there will be references to both cubic and hexagonal (four index) Miller notation. Four index Miller notation is well described in literature [96, 97], but for simplicity Figure 1.8 outlines the relevant Miller directions for a III-As nanowire in both polytypes, assuming it is grown along the $\langle 111 \rangle$ (cubic) or $\langle 0001 \rangle$ (hexagonal) equivalent direction. The **a** axis ($\langle 01\bar{1} \rangle / \langle \bar{2}110 \rangle$) and **m** axis ($\langle 11\bar{2} \rangle / \langle 1\bar{1}00 \rangle$) are typically aligned with the nanowire facets and

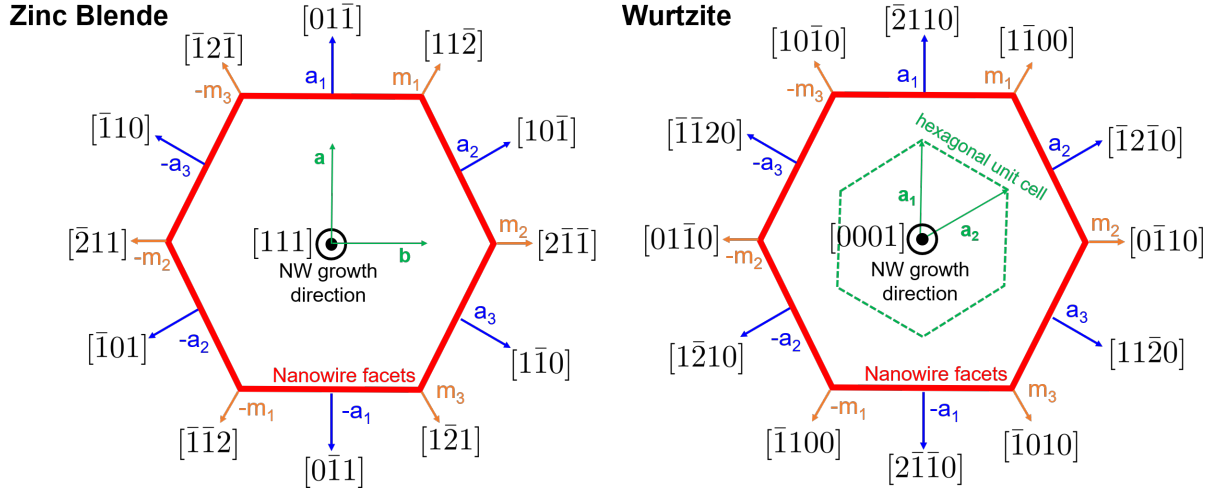


Figure 1.8. Miller directions for the equivalent ZB (cubic) and WZ (hexagonal) III-As nanowires using (hkl) and four-index (hkil) miller notation respectively. Corner facets are described as **m** facets and the hexagon sides as **a** facets.

corners as shown. For crystals of mixed polytype phase, this thesis will utilize the cubic ZB Miller notation, unless stated otherwise.

1.4.4. Strained interfaces in III-As heterostructures

Much of the discussion thus far has been of GaAs and AlGaAs nanowires, because they are the most well developed class of III-As nanowires. GaAs is often used as a nanowire core because it can be grown very controllably. Further, GaAs nanowires have been shown to act as a good gain medium and optical cavity for low-threshold lasing [98]. Growing AlGaAs QWs on GaAs cores combines the improved gain from the AlGaAs QWs with the efficient optical cavity of the GaAs core [51, 99]. This GaAs/AlGaAs quantum heterostructure utilizes a nearly ideal materials combination. First, AlGaAs has a tunable emission from ~ 1.77 eV for $\text{Al}_{0.47}\text{Ga}_{0.53}\text{As}$ to 1.42 eV for pure GaAs (AlGaAs becomes indirect at an Al content greater than 47%) [4]. This range of tunable emissions is shown in Figure 1.1. Additionally Ga and Al have similar radii ($1.87 \text{ \AA}$ vs. $1.84 \text{ \AA}$) so there is minimal lattice mismatch between GaAs and AlGaAs regardless of the Al content, as demonstrated in Figure 1.9. This means that there is negligible strain at the GaAs-AlGaAs interface in these quantum structures. As such much research has been done

in the area of AlGaAs/GaAs core/shell nanowire lasers. This heterostructure has even demonstrated optically pumped lasing up to room temperature [51].

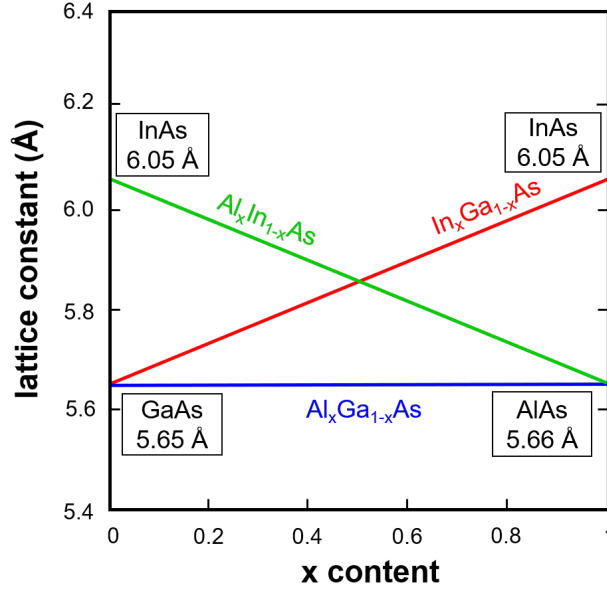


Figure 1.9. Lattice parameter (Å) as a function of composition (x- content) for ternary compounds of GaAs, InAs, and AlAs.

However, this emission between 550-815 nm is far from the near-IR telecommunication band (1260-1625 nm) necessary for on-chip optical communications and minimizing absorption losses to Si waveguides [5]. This need for telecom band communication motivates the switch to InGaAs alloys which offer emission up to 3500 nm for pure InAs (see Figure 1.1).

Pure InGaAs nanowires have been grown in attempts to produce telecom lasers, but catalyst assisted (VLS) growth results in composition gradients both along the nanowire length and radially [100, 101]. Catalyst-free (VS) grown InGaAs nanowires can be grown with uniform composition, but are challenging to grow beyond a few microns in length due to their self-terminating growth [102, 103]. This optical cavity length is too short to produce lasing (typically 5-15 μm is necessary) [104].

The primary challenge that makes GaAs/InGaAs core/shell heterostructure more complex than the well studied GaAs/AlGaAs heterostructure is the large lattice mismatch between GaAs and InAs. The difference in lattice parameter between InAs and GaAs is shown in Figure 1.9 as a function of In content.

In their binary forms, it is not possible to grow InAs films on GaAs substrates because this would result in a -7% strain, leading to three-dimensional growth of InAs islands. Even InGaAs with only 20% In results in a -1.5% strain if interfaced with GaAs. This large mismatch can greatly modify the growth, even in nanowire heterostructures. For instance, Balaghi et al. determined that for a small GaAs core (diameter of ~ 25 nm) coherent growth of InGaAs shells was possible up to 55% In, but beyond 55% misfit dislocations occur between the core and shell [105, 106]. Further, Yan et al. simulated that for GaAs/InGaAs/GaAs core-shell-shell nanowires with an In content of 20%, dislocations may occur if the InGaAs shell thickness exceeded 22 nm (though this is for perfectly cylindrical heterostructures) [107]. Growth of InGaAs shells often results in lower In content in the shell than predicted, as strain is another driving force that inhibits In incorporation [108]. Strain is known to cause modifications in morphology during growth and prevent or modify incorporation of dopant species [109, 110].

Strain can also modify the band structure of III-As materials, shifting the conduction band and valence band offsets [111, 112]. This phenomenon was studied decades ago in GaAs/In_{0.2}Ga_{0.8}As superlattice films grown as strained-layer superlattices, where strain engineering was used to modify the band offsets, polarization, and hole transport [113, 114, 115]. Strain in thin films is easy to predict and measure, thus the effects on growth and device properties can be reasonably predicted. The same cannot be said about nanowire heterostructures due to their complex geometry and the difficulty of resolving strain at the nanoscale. Some of the challenges involved in predicting and confirming strain within III-As nanowire structures will be addressed in this thesis, starting with a comparison of strain calculations for thin films and strain modeling in nanostructures in Section 2.5.5. Ultimately, it is critical to understand the nanoscale strain state of III-As nanowire heterostructures to enable the same type of strain engineering that has been done in thin films superlattices and to prevent defects/strain from causing degradation of electronic and optical properties.

1.4.5. Need for 3D correlative total tomography

In this chapter, the potential of GaAs/InGaAs nanowire heterostructures as compact emitters for on-chip telecommunication has been discussed. However, the complexity of inherent to these structures has thus

far prevented them from achieving efficient near-IR emission. There is a need for better understanding of the interplay between composition, morphology, strain, and polytypism within single nanowires. However, since these nanowires are comprised of embedded quantum structures or buried dopants, common surface or 2D characterization techniques are insufficient to understand what structural components are dictating the device properties. Instead, we are in need of a suite of 3D characterization techniques that can probe buried structures in a correlative fashion. As demonstrated in this section, simply knowing the composition of a single wire is insufficient for explaining the optical properties. Instead, composition, strain, polytypism, and morphology must be correlated with one another, as they all can effect each other during the growth process. Further, structural and compositional information must be correlated directly, when possible, to electronic/optical measurements of the heterostructure, as a change in any structural feature has the potential to modify the optoelectronic behavior of the nanowire.

CHAPTER 2

Tools for Single-Nanowire Total Tomography

This chapter addresses the need for three-dimensional tomographic imaging in nanostructures and the need for correlative characterization of nanowire heterostructures. An overview is given of the characterization techniques used in this thesis for such correlative or tomographic analysis. This includes atom probe tomography for dopant and composition mapping in 3D and electron imaging for structural and compositional analysis. An overview of the finite element modeling necessary for correlating composition and structure to strain is given. Section 2.4 introduces a few synchrotron-based X-ray imaging techniques that are used for strain analysis in this work. Finally, a brief overview of some electrical and optical characterization techniques is given.

2.1. Why is Correlative Tomographic Imaging Required?

Most often, nanowires are measured as an ensemble, where tens to thousands of wires are simultaneously probed to gain understanding about their composition or properties. This can be very useful when studying highly uniform nanowire arrays or when trying to gain a high-level understanding of variations in behavior between nanowires in the ensemble. For instance, in photoluminescence (PL) measurements of InGaAs nanowire ensembles, Shin et al. observed broadening and a slight shift in the PL peak. This observation was used to hypothesize the presence of In fluctuations (inducing broadening) and the presence of a WZ phase (inducing the peak shift) [116]. While this is a useful analysis that gives insights into the behavior of these nanowires under certain growth conditions, it leaves a lot of room for interpretation. In nanostructures with even more complexity than these pure InGaAs nanowires, the level of ambiguity increases, meaning minimal conclusions can be drawn from this type of ensemble measurement. Single nanowire measurements can alleviate some of this ambiguity, as variations between individual wires are no longer convolved with one another. As such, much effort has been made in characterizing properties of

individual nanowires. This includes efforts in single nanowire spectroscopy [117, 118], micromanipulation to isolate individual nanowires [119, 120] and developments in single nanowire device fabrication [121].

Single nanowire measurements are often useful, and will be utilized in this work, but in some cases spatial sensitivity on the single nanowire scale is also required. As an example, in [122], Dick et al. utilized HAADF-STEM and X-ray energy dispersive spectroscopy (EDS) to map the composition across the length of an InAs/GaAs axial heterojunction nanowire. In this way they were able to determine how abrupt a junction they had grown. Simpler techniques like Raman spectroscopy would have been able to infer an average composition in the nanowire or even spatially at a few points on the wire (with an $\sim 2 \mu\text{m}$ step size), but this information would be insufficient to probe the composition at this sharp junction. As in this example, highly spatially resolved characterization techniques are often needed to fully characterize a nanowire heterostructure.

As introduced in Section 1.4.5, the 3D nature of nanowire heterostructures requires characterization techniques that can probe buried interfaces. This is a non-trivial requirement, especially given the nanometer scale at which structural features may vary. Thus nanostructure characterization often requires three-dimensional imaging techniques. Some techniques that are useful for 3D, highly spatially resolved characterization will be outlined in this chapter. In this thesis, such highly resolved characterization techniques will be used in a correlative fashion, using two or more characterization techniques on a single nanowire. In this way, structure-property relationships can be obtained and the growth process of the nanowires can be better understood. In the ideal case, all characterization could be performed on the same nanowire, and many nanowires would be measured to fully understand what variations may occur between wires. However, given the challenging nature of many of the characterization techniques presented in this chapter this is not always possible. If correlative analysis can be performed on a few single nanowires, this is considered a success at the current development level of these techniques. Further, if all characterization techniques cannot be performed on the same exact nanowire, it is even more important to get an understanding of how much variation there is between nanowires in the growth. This approach, which we refer to as ‘Total Tomography’ aims to understand the structural details of single III-As nanowire heterostructures, in order

to feedback to the growth process what should be modified to grow an optimal nanowire emitter.

2.2. Atom Probe Tomography for 3D Composition Mapping

The primary tool for compositional imaging in this work is atom probe tomography (APT). APT is a successor of the field ion microscope (FIM) which was developed in the 1950's by Erwin Müller [123]. FIM was the first experimental method capable of resolving individual atomic columns, which was demonstrated by Müller using a tungsten (W) tip. By forming a large electric field on the surface of a sharpened W tip through the application of a high voltage (5-20 kV), and pumping into the vacuum chamber a helium imaging gas, the W ions could be “torn off” the surface of the tip, imprinting the image of the atomic surface onto a phosphor screen [124]. This eventually was discovered to be the result of field evaporation. Field evaporation is the process of removing an atom from the surface of a material due to their bonds rupturing from the presence of a large electric field [125]. Thus APT is a destructive technique, and must always be performed last in the order of correlative analysis.

In the 1980's M.K. Miller introduced the three-dimensional atom probe, which allowed for single atom detection on a microchannel plate, allowing for position sensitive detection [126]. Using this tool, successive layers of atoms are field evaporated, leading to the ability to generate 3D maps of composition in a specimen. In the years following numerous additions were made by Miller and others, including the introduction of a local electrode and a laser pulsing system, that led to the modern local electrode atom probe (LEAP) [127]. In addition to the atomic scale resolution made possible by FIM, modern LEAP has a part-per-million (ppm) chemical sensitivity at the appropriate conditions, thus making it a uniquely useful tool for mapping dilute species in 3D structures.

2.2.1. Basics of LEAP

During LEAP, a needle-shaped specimen is loaded into a UHV chamber and cooled to cryogenic temperatures (< 100 K). A standing voltage (V_s) is applied to the specimen (2-30 kV) and the tip is aligned in close proximity with a counter electrode. Upon a voltage pulse (V_{pulse}) or laser pulse a single ion should

field evaporate from the tip surface and then accelerate towards a time-of-flight (ToF) single-ion detector which is position sensitive in the detector plane, giving the detector positions (X_d, Y_d) . The ion mass-to-charge ratio (m/n) is determined by calculating the time-of-flight (between the laser or voltage pulse and the ion impact on the detector). The mass-to-charge ratio gives insight into identity of the evaporating ion. After many millions of laser/voltage pulses are applied, thus millions of ions have been evaporated from the surface, the Z-position of these ions can be determined based on the order of evaporation. A schematic of this process is shown in Figure 2.1.

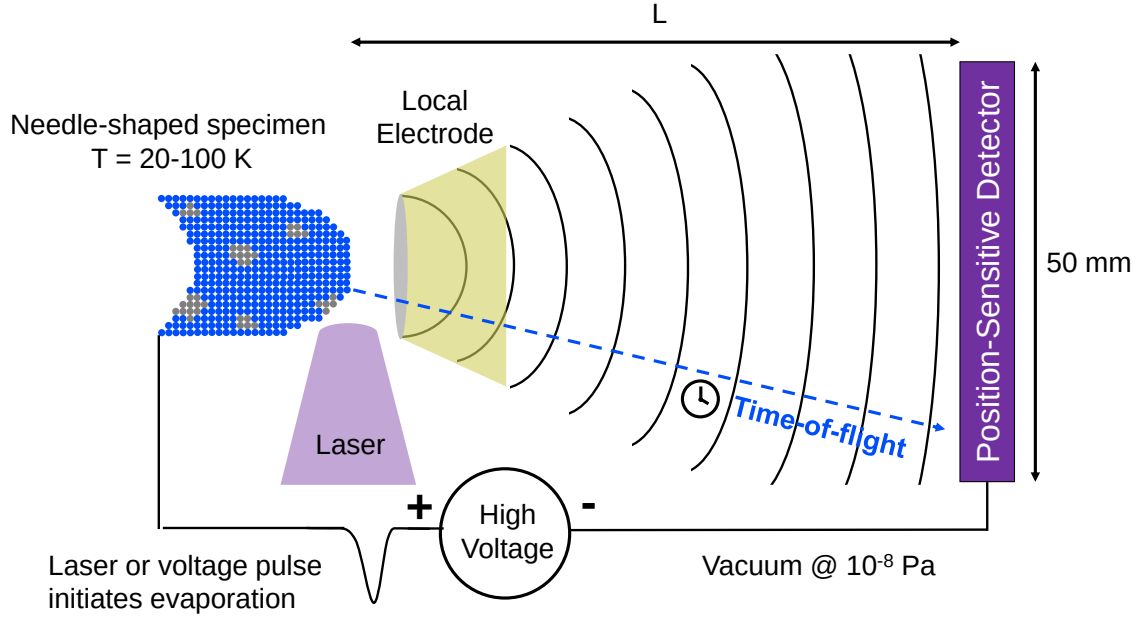


Figure 2.1. Schematic of local electrode atom probe tomography. Adapted with permission from Saxey, D. W., et al. Scripta Materialia 148 (2018): 115-121. Copyright © 2018 Acta Materialia Inc. Published by Elsevier Ltd. [128]

After APT analysis is complete, the 3D atomic map of the specimen is reconstructed. The X and Y positions of the ions are calculated as the detector positions (X_d, Y_d) divided by a magnification factor (η), given by

$$\eta = \frac{L}{\xi r_t}$$

where L is the distance between the specimen and detector (as shown in Figure 2.1), ξ is the image compression factor, and r_t is the specimen radius of curvature. The parameter L is approximately known and the radius of curvature is either measured from the sample or estimated using the evaporating voltage (V), an estimate of the evaporation field at the specimen tip (F) and an estimated geometrical field factor (k), according to the equation:

$$r_t = \frac{V}{kF}$$

However, the image compression factor and sometimes the radius of curvature are ambiguous. During atom probe reconstruction, most often other known features are utilized to estimate ξ and r_t , such as the known atomic spacing along a certain crystallographic pole, landmark tracing (such as using the known spacings between layers of different composition in an atom probe sample), or by knowing the diameter along the length of an APT tip and the amount of material evaporated (such as from performing SEM before and after evaporation). In the final reconstruction, though atomically resolved, about 20-50 % of the atoms will be missing because the ToF detector has only a 50-80 % detection efficiency (depending on the LEAP model). For more details on atom probe measurements and the reconstruction process see references 127 and 126.

2.2.2. APT of Semiconductors

FIM and APT were designed to be performed on metals such that large enough electric fields could be conducted to the tip surface for field evaporation. However, with the introduction of laser-assisted APT (LA-APT), researchers began to explore a broader range of materials for analysis by APT. In LA-APT, a standing voltage is still applied to the specimen tip, but instead of a voltage pulses, ultra-fast laser pulses are used to heat the specimen, providing sufficient thermal energy for ion field evaporation [129]. Due to the large voltages needed for voltage-pulse APT this method often results in fracture or low resolution mass spectra in non-conducting or semiconducting samples. Thus, in this work only LA-APT will be utilized.

There are only a few parameters available for modification during APT analysis: laser power, laser pulse rate, stage temperature, and targeted detection rate. To minimize uncorrelated evaporation between

laser pulses, the tip is kept at low temperatures, typically < 30 K for semiconductors. The target detection rate is the percent of laser pulses for which an ion is evaporated/detected, typically 0.5-5%. For III-As semiconductors, a typical laser pulse energy and pulse rate would be 0.01-5 pJ and 250-500 kHz. For a given laser power and pulse rate, the detection rate is a metric of the average electric field on the tip surface and should remain constant during evaporation. As such the standing voltage is automatically adjusted to maintain the target detection rate under changing samples conditions (such as tip diameter or changing evaporation fields from varying tip composition). For semiconducting samples, the voltage is typically kept under 5 kV, for which the chances of catastrophic tip fracture are high.

One main challenge in APT measurements is properly balancing the laser pulse energy and the standing voltage. Too high of a standing voltage means there will be significant uncorrelated evaporation events, but too high of a laser pulse energy means that there may be surface migration of atoms before field evaporation or preferential evaporation of a particular species. This is especially true for III-V materials that see preferential evaporation of group-III species at higher laser pulse energy [130, 131]. This becomes more challenging in non-uniform alloys, such as the ternary III-As heterostructures studied in this thesis. One way to determine the correct balance between the laser pulse energy and voltage is to utilize knowledge from previous successful APT runs of similar composition and structure. Since no APT tip will be of uniform shape and curvature, the best way to directly compare between runs is using ion charge-state ratios. Charge-state ratios refer to the ratio of the counts of the same element at different charge states, for example As^{2+} counts/ As^+ counts. Charge-state ratios give an estimate of the local electric field on the tip surface. In previous work by Jeon et al. on APT of GaAs/AlGaAs QW heterostructures, for high quality APT measurements typical $\text{Ga}^{2+}/\text{Ga}^+$ and $\text{As}^{2+}/\text{As}^+$ charge state ratios were 10^{-3} and 10^{-1} respectively [132]. These charge state ratios were utilized in this work to choose appropriate starting parameters for APT of GaAs/InGaAs QW heterostructures. It is also important to compare atom probe measurements to other techniques, such as STEM, to confirm the validity of the compositional analysis.

2.2.3. Interpreting APT measurements

An example 3D atom probe reconstruction of an InAs nanowire is shown in Figure 2.2 along with the corresponding mass spectrum. The mass spectrum is a histogram of all the evaporated species in the reconstruction as a function of their mass/charge ratio (in units of Daltons, Da). In this mass spectrum, a few peaks are labeled with the assigned ion species.

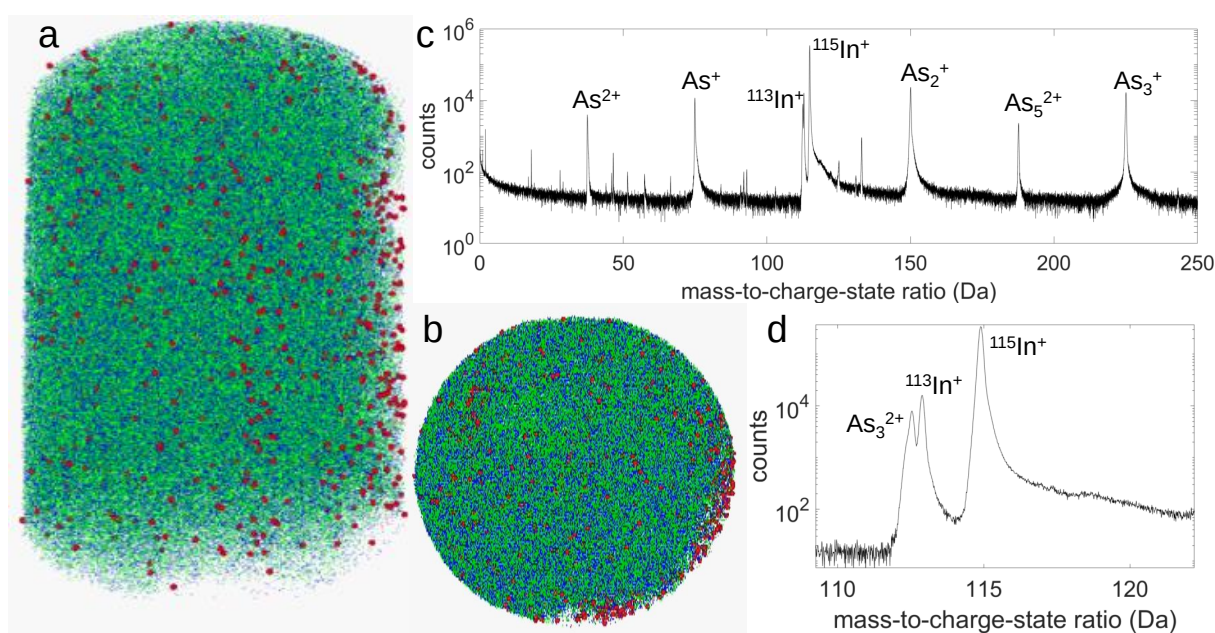


Figure 2.2. Example of APT reconstruction and mass spectra. 3D reconstruction of InAs nanowire shown along the reconstruction length (a) and from the top (b). Dots in the map are individual ions. Indium atoms are shown in blue, arsenic atoms are shown in green, and Si-dopants are shown as red spheres. (c) The corresponding mass spectrum for this reconstruction. Select ion species are labeled next to their peak, arsenic of multiple molecular species (As_2 , As_3) and arsenic of varying charge state (As^{2+} , As^+) are shown. Two different indium isotopes (113, 115) are present. (d) A magnified plot of the mass spectrum. The two indium isotopes are more clearly seen, along with an arsenic molecular species overlapping with the In-113. A low noise level to the left of As_3^{2+} at 112 Da is seen. A long thermal tail from the In-115 peak is seen continuing past 120 Daltons.

It is critical to identify the ion species in order to create an accurate 3D atomic map. There are instances where the mass/charge of multiple ions overlap, causing ambiguity in the identity of an ion.

For instance, $^{14}\text{N}^+$ and $^{28}\text{Si}^{2+}$ both occur at 14 Da, thus without prior knowledge of the APT sample the ion type is difficult to determine. For this reason, it is important to anticipate when preparing a sample what ion species may have overlapping mass/charge ratios. It is also common during APT that ionic species can evaporate as molecular species (such as Al_3^+) or complex ions (such as AlSi^+ or SiO^+). Certain species have multiple isotopes, such as ^{115}In and ^{113}In as seen in Figure 2.2, and will evaporate in ratios proportional to their known earth abundances. Multiple ions are known to evaporate at the same time, but this “multiple evaporation” event should be minimized by modifying the pulse power or voltage. Uncorrelated ion evaporation, or evaporation that occurs between laser/voltage pulses result in uncorrelated background counts within mass spectra. This background level, as seen for example to the left of In_3^{2+} at 112 Da in 2.2(d), is subtracted from the mass spectra before calculating the number of counts for each ion type. If this background level is too high, it can prevent the detection of dilute species. In LA-APT, broadening to the right of large peaks is often observed (seen to the right of ^{115}In in 2.2(d)). These are known as thermal tails, and result due to slow cooling of the tip due following the laser pulse. As with uncorrelated evaporation, the large broadening can prevent detection of dilute species if the species peak lies within a thermal tail. It is therefore important to anticipate where peaks of interest will fall with respect to one another before conducting an atom probe measurement.

The evaporation of structures containing multiple materials (such as nanowire heterostructures) can result in additional challenges or artifacts that must be taken into account. First, for a tip containing materials A and B of two different evaporation thresholds, if the high evaporation field material A is evaporated first, evaporation conditions must allow for evaporation of material A, but when the interface of material B is exposed, the evaporation rate may increase rapidly since conditions are set to evaporate material A. A burst of evaporation can result in tip fracture. Additionally, if the interface between materials A and B runs parallel to the tip length, thus they are both evaporating at the same time, the differences in evaporation field and result in local changes in tip curvature. This curvature, due to the difference in evaporation rates between the two materials, will lead to ions evaporating along ambiguous trajectories (deviating from the ion projection of a perfectly hemispherical tip). Thus when reconstructing the APT data, the X and Y positions of ions will not be perfectly determined. Specifically,

within the regions of lower evaporation field, ions will evaporate more quickly, causing a locally concave evaporation front, resulting in trajectories that reduce the magnification of the lower evaporation field material. This trajectory overlap effect between high evaporation field and low evaporation field materials is difficult to deconvolve after the APT measurement [133]. In these complex heterostructures, a perfect 3D composition map is impossible to achieve, so ultimately it is most important that APT conditions are chosen and samples are prepared in a way that will allow the most critical information to be extracted from the data. The general metrics of a quality APT run for nanowires is discussed in detail in reference 134.

2.2.4. Sample preparation of nanowires for APT

Atom probe requires that materials be formed into very sharp tips (~ 100 nm) in order to produce a large enough electric field for field evaporation. Tip preparation is possibly the most important and most challenging aspect of atom probe tomography. Traditionally for APT of bulk metals, electrochemical polishing (electropolishing) is performed by putting a wire-shaped metal sample in an electrolyte bath, while attached to an anode and applying a DC current. Acting as the cathode material, the metal sample oxidizes and the surface atoms are dissolved into the electrolyte. This process removes material at the meniscus of the electrolyte bath until the wire breaks in two pieces, one end being finely sharpened [135, 136]. This of course requires the sample be conductive in order to act as the cathode, additionally if a sample is inhomogeneous, this leaves no flexibility to form the tip in a particular region of interest within the sample. Thus most APT sample preparation now occurs using a dual beam scanning electron microscope (SEM)/ focused ion beam (FIB). FIB milling utilizes Ga^+ ions to locally mill away material. In bulk materials, a lift-out method has become common for creating APT tips from a region of interest.

An overview of the lift-out process is seen in Figure 2.3. Before lift-out, a protective layer must be deposited on the substrate in order to protect the material from Ga^+ beam damage or re-deposition of milled material onto the substrate ROI (2.3(a)). Protective films can be deposited prior to loading into the SEM/FIB or a protective layer of carbon or Pt can be deposited using the electron or ion beam. Typically, some amount of Pt is deposited in FIB for protection and as a marker for aiming the wedge

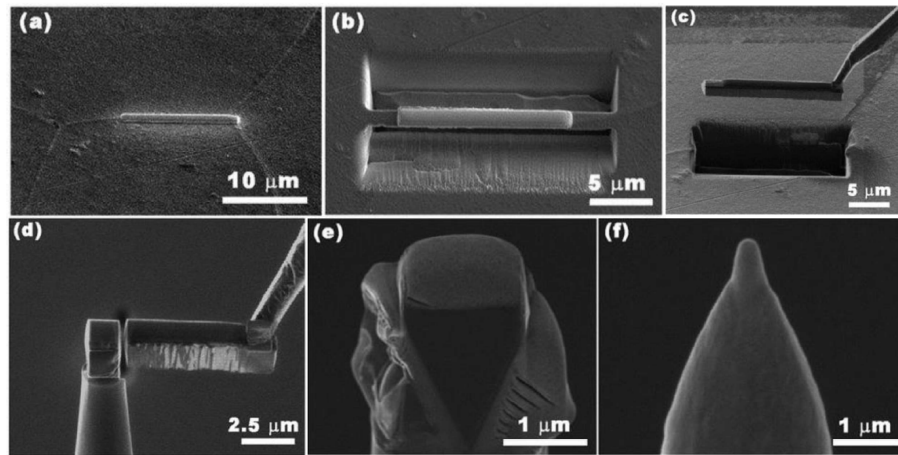


Figure 2.3. FIB lift-out procedure shown by SEM images. (a) A protective carbon or Pt layer is deposited, (b) then angled cuts are milled to form a wedge. (c) The wedge is attached to a micromanipulator using Pt deposition and cut completely out from the bulk substrate. (d/e) The edge of the wedge is attached to a Si micropost and cut from the rest of the wedge. (f) The wedge is sharpened into a fine point ready for APT analysis. Adapted with permission from Devaraj, Arun, et al. *International Materials Reviews* 63.2 (2018): 68-101. Copyright © 2018 Taylor & Francis. [137]

cut. Next, as seen in 2.3(b), angled cuts are made around the ROI. A cut is then made to remove one edge of the wedge from the substrate (not shown). A micromanipulator tip is then welded to the edge of the wedge region using Pt and the edge cut is made to remove the wedge from the substrate (2.3(c)). Next, (2.3(d)) using the manipulator the wedge is aligned and the edge is welded onto the top of a Si micropost tip. Figure 2.3(e) shows the wedge mounted and Pt welded onto the micropost. The wedge is then milled into a fine tip using lower energy annular FIB milling (2.3(f)). Multiple tips can be formed from each lift-out segment. Much work has been done in designing lift-out and milling procedures to create tips of various widths and curvature depending on what is required for APT. For an overview of this process please see the reviews in Ref. 138 and 137.

This lift-out procedure has been adapted for analysis of nanostructures/nanowires whether in their epitaxial geometry or redeposited onto a substrate. For instance, Blumtritt et al. performed APT of individual Si nanowires (length ~ 200 nm) via lift-out from the original growth array [139]. In this case, a Ni layer was sputtered onto the nanowire array and an additional Pt layer was deposited prior to lift-out as a protection layer. A wedge of the substrate including a few nanowires was cut out, a single

nanowire segment was mounted onto a Si micropost and the protective layers were milled away. In another example of nanowire lift-out, Sun et al. used a conformal atomic layer deposition coating of ZnO to both protect and adhere Si nanowires onto the Si substrate on which they were transferred (but not epitaxially attached) [140]. As the adhesion layer was not fully removed during milling, ZnO was chosen to minimize the difference in the field evaporation threshold between the nanowire and coating to reduce artifacts and minimize the risk of tip fracture as discussed in Section 2.2.3.

Since the nanowires explored in this thesis are generally between 80-150 nm in diameter, single nanowires are already in the appropriate needle-shaped geometry. So the primary tool for APT tip preparation here will be micromanipulation to isolate single nanowires. The two techniques that will be utilized are discussed in detail in Appendix A: nanowire pick-up and direct pick-and-place. In summary, these techniques require the nanomanipulation of individual nanowires using a tungsten manipulator tip in SEM/FIB. While nanowire pick-up is more direct and higher yield than direct pick-and-place, direct pick-and-place is necessary when selection of a particular nanowire is required (such as for correlated measurements). While isolation of single nanowires is a low yield process (30%), it produces fewer artifacts for APT analysis of nanowires compared to coating and lift-out. This is because no secondary material is needed to coat the wires and the nanowires are typically untapered, meaning the narrow diameter continues for many microns away from the tip apex.

2.2.5. Summary: atom probe tomography

In summary, atom probe is a uniquely powerful tool for compositional mapping of 3D structures. While it is best suited for analysis of conductive materials, advances in laser-assisted atom probe have allowed for useful information to be extracted from semiconducting and insulating samples. APT analysis of semiconducting specimen is a challenging endeavor and critical consideration must be given to potential reconstruction artifacts. Despite its challenges and limitations, APT has proved to be an extremely useful tool for probing the composition and morphology embedded within III-As nanostructures, as well as investigating the presence of dilute species like dopants.

2.3. Electron Microscopy for Probing Structure, Composition, and Strain

While X-ray imaging is the primary structural analysis tool used in this thesis, electron imaging is an invaluable tool for imaging crystal structure, composition, and even strain in nanostructures. In this work, electron imaging is often used in correlation with atom probe or X-ray imaging. In this section an overview of some electron microscopy techniques is given and limitations of these techniques are addressed.

2.3.1. Scanning electron microscopy — imaging, spectroscopy, and diffraction

Scanning electron microscopy (SEM) is used throughout this thesis for imaging the morphology of nanowire arrays and mapping the location of single nanowires prior to micromanipulation or X-ray imaging. See Appendix A for more details. Along with direct imaging via collection of surface scattered electrons, secondary X-rays can be collected from the material surface in SEM to map composition via energy dispersive X-ray spectroscopy (EDS). EDS is broadly useful for qualitative elemental imaging in materials. Quantitative composition analysis is non-trivial, requiring correction for absorption, secondary fluorescence, and background radiation, however recent advances in EDS detectors has made this process increasingly common [141].

In addition to elemental analysis, an SEM can be used for mapping crystal phase and orientation using back-scatter diffraction. This method, known as electron back-scatter diffraction (EBSD), involves placing a sample at a steep tilt (typically 70°) relative to the incident high-energy electron beam, and recording the diffraction from the sample surface on a phosphor screen in close proximity. Diffraction patterns known as Kikuchi patterns are formed of numerous bands that intersect at zone axes. Indexing of Kikuchi patterns, which can typically be done automatically (using an EBSD indexing software), can predict the corresponding crystal phase and crystal orientation at a single spot. The electron beam scans across the sample to create line profiles or spatial maps of orientation with typically 10-50 nm spatial resolution (depending on the beam conditions and sample). It is critical for EBSD that samples have clean surfaces, as the secondary electrons only escape from about 20 nm or less, so often plasma cleaning or polishing is performed on the sample prior to EBSD [142]. More advanced EBSD techniques have

been developed to image structure in 3D. 3D EBSD is done by collecting maps of Kikuchi patterns from a material surface then FIB milling the top surface away to reveal a new surface below. Imaging and milling are performed consecutively until the sample has been destroyed. From this analysis, 3D images of the crystal structure and orientation can be generated. 3D EBSD is not done regularly as it is extremely time consuming and requires an SEM/FIB dual-beam systems with an EBSD detector [143, 144].

2.3.2. Conventional and scanning transmission electron microscopy

Transmission electron microscopy (TEM) involves using a higher energy beam (60–300 keV compared to 1–30 keV for SEM) to penetrate through thin specimen. In TEM, electrons are collected in transmission instead of reflection as in the case of SEM. The high beam energy used in modern TEM enables focusing to very small spot sizes with electromagnetic lenses [145]. Advances in electron sources and focusing components over the last couple decades have greatly improved electron beam coherency and reduced spherical aberrations. Such improvements have widened the possibilities for experimentation using electrons and improved the spatial resolution of the best TEMs to better than 0.1 nm (smaller than many inter-atomic distances) [146]. Thus images of the atomic structure in a crystal can be obtained via high-resolution TEM (HRTEM), though this technique requires detailed sample preparation and expert TEM operation to resolve individual atomic planes. Further, HRTEM has a limited field of view (tens of nanometers), is limited to very thin samples, and traditionally produces only a 2D image which can be complicated by projection effects [147].

To investigate crystalline samples in TEM, selected area electron diffraction (SAED) is commonly used. Given the small wavelength of an TEM beam (in the range of 0.2–0.04 Å), diffraction from the lattice will occur. An SAED pattern contains many diffracted spots corresponding to different diffraction conditions. These patterns can be indexed to determine crystal structure, orientation, and lattice parameters. Common imaging techniques within TEM include amplitude contrast imaging, diffraction contrast imaging, and phase contrast imaging. Within each of these imaging schemes a bright field (BF) and dark field (DF) pattern are collected by imaging either the diffracted beam or transmitted beam. The BF and DF give complementary images, higher brightness for BF and higher contrast for DF, allowing different

sample features to be resolved. Amplitude contrast imaging gives contrast due to thickness variations or Z (atomic number) by probing the incoherent elastic scattering of electrons from the sample. In diffraction contrast imaging, the specimen is tilted to a *two-beam* condition, at which a singular diffraction condition is dominant (instead of many as in SAED for amplitude contrast imaging). Notably, diffraction contrast probes the coherent elastic scattering from the sample, revealing which regions of the sample fulfill the selected diffraction condition and which do not. Diffraction contrast can be used to image dislocations or stacking defects within a sample. Finally phase contrast imaging differs from the previous techniques in that it utilizes multiple beams simultaneously to produce beam interference patterns. These interference patterns produce lattice fringes that provide information about lattice spacing and orientation which can be used to generate lattice images. However, these lattice images must be interpreted carefully as they are not direct atomic images. Another common phase contrast result is Moiré patterns, which are interference patterns generated by nearly parallel periodic arrays. Moiré patterns are the result of slight crystal misorientation or atomic misfit at interfaces. Therefore, phase contrast can be used to investigate heterostructures or low-angle polycrystalline materials. See reference 148 for a detailed review of the previously discussed imaging schemes and other less common imaging modes in TEM, as well as for tips on practical TEM measurements and analysis.

Scanning transmission electron microscopy (STEM) is a type of TEM in which the incident beam is focused and scanned across the sample. STEM images are not magnified based on the lenses after the sample as in TEM, but instead are magnified maps of the scanned region. STEM offers many of the same imaging schemes as TEM (diffraction, phase, amplitude contrast), but also opens more imaging possibilities given the scanning capability and additional detectors placed below the sample. The added capability includes annular dark field (ADF) imaging and high angle annular dark field (HAADF). ADF collects complementary BF-like images and HAADF collects more high angle scattering (such as Rutherford-scattering) which minimizes diffraction contrast and creates more interpretable Z -contrast images. For more details, see Part 1 and 2 of reference 148.

2.3.3. Strain imaging with electron microscopy

There are a few TEM/STEM techniques used to measure strain. These include dark field electron holography (DFEH) and geometric phase analysis (GPA) of images from HAADF STEM, nanobeam diffraction (NBED), and precession electron diffraction (N-PED). For more details on these techniques, see Reference 149. While these are powerful, highly spatially resolved techniques for strain analysis, each comes with limitations. DFEH and N-PED offer very high strain resolution (0.05%) with a few nm spatial resolution. However, in DFEH the quality of the sample greatly limits the strain precision and N-PED is extremely time consuming in both collection and data processing. HAADF STEM offers the best spatial resolution (down to 1 nm) but is limited in strain resolution ($\sim 0.2\%$ strain). NBED offers slightly better strain resolution ($\sim 0.1\%$) but lower spatial resolution (~ 5 nm) and often produces inaccurate results due to variations in diffraction spot intensity. At this point, N-PED is perhaps the best electron-beam based method for measuring nanoscale strain with high accuracy, but is time consuming and requires a TEM with electron beam precession. In addition, thick samples, such as nanowire heterostructures, must be thinned, which can induce damage and modify the strain state. Additionally, these techniques are all 2D projections of the strain, so complex heterostructures are difficult to measure. For instance, if a cross-section of an InGaAs nanowire QW is imaged in STEM, any variations in QW width or composition across the cross-section thickness will be convolved in a single 2D strain map [150, 149, 151].

2.3.4. Elemental analysis in TEM/STEM

Similar to EDS analysis for SEM, discussed in Section 2.3.1, elemental analysis is possible using conventional TEM or STEM. Using EDS, chemical mapping of a sample can be performed down to the atomic scale in STEM. EDS-STEM is commonly used for elemental mapping and contrast imaging of nanostructures, with a sub-nm resolution [152]. Alternatively electron energy loss spectroscopy (EELS) is a technique used for elemental mapping in TEM/STEM that measures the change in kinetic energy of electrons after they interact with the sample [153]. In comparison to EDS, which is best for heavy element identification (above Li), EELS is more suitable for light element identification. EELS is more difficult than EDS, as it requires detailed spectra analysis and even thinner samples (< 80 nm). However,

EELS offers higher spatial resolution than EDS and additional information about chemical bonding, valency and electronic properties. As discussed for TEM, EDS and EELS maps are a projection of the 3D sample and require sample thinning, making them non-ideal for analysis of complex 3D heterostructures. Additionally, these high resolution imaging techniques, especially EELS, are extremely sensitive to surface contamination (usually carbon). Often plasma cleaning or ion milling is used to remove contamination immediately prior to electron imaging. However, for sensitive materials such as InAs and InGaAs, plasma cleaning can lead to significant oxidation or sample damage. GaAs in general is robust to moderate oxygen plasma cleaning, as gallium oxides do not form readily. Finally, the chemical sensitivity of electron spectroscopy is not as high as that of APT, generally preventing the detection of dopant species. However, EELS and particularly EDS act as highly complementary techniques to APT. They can be used to confirm the accuracy of APT experiments, and often have better composition accuracy in III-As heterostructures [154, 155].

2.3.5. Electron imaging in three-dimensions

The focus of this thesis is 3D mapping using atom probe and X-ray imaging. It is therefore relevant to consider what type of 3D imaging can be performed using electron microscopy. Though some of the electron microscopy techniques mentioned previously can probe buried interfaces (such as by milling cross-sections of samples), all of them are 2D projections of a 3D structure. However, electron microscopy techniques have been created that allow for high-resolution structural and chemical analysis of materials in 3D.

First, electron tomography allows for 3D maps of sample morphology, which is useful for investigating precipitate distributions and 3D nanostructures. Electron tomography involves taking a STEM Z-contrast image, rotating the sample $1\text{-}2^\circ$ and repeating the STEM measurement. Most STEM tilt holders do not possess full 360° rotation capability, as such there is often a missing wedge of information in the data set. However, for most samples common $\pm 70^\circ$ tilt holders are sufficient to reconstruct the object shape/size without significant artifacts [156]. This 3D analysis has been extended to EDS-STEM and EELS, sometimes referred to as 4D-STEM. These techniques involve 3D STEM mapping using a tilt series,

but also record the EDS or EELS spectra (hence, 4D). These allow for nanometer scale spatial resolution and are ideal for complex heterostructures that require 3D analysis for appropriate interpretation as in the example by Lepinay et al., where the 3D composition of a 28 nm transistor was mapped using 4D EDS-STEM [157]. In addition to elemental analysis, 4D EELS has been used to map differences in Si-bonding within a Si/metal contact structure and electronic properties in a ZnO/Au matrix [158]. Though there have been some examples of dopant mapping using EDS/EELS in 2D and 3D [159, 160, 161], these techniques do not compare to the high chemical resolution of atom probe tomography.

Beyond tomographic imaging, 3D electron imaging can be done using ptychography. Ptychography, which will be discussed in more detail in Section 2.4.3.1, involves scanning a probe in overlapping steps on the sample. Ptychography combined with an inverse multi-slice method allows for 3D reconstructions of sample morphology or Z-contrast without the need for large sample tilts. This allows for more flexible sample geometries and compatibility with *in-situ* sample holders, such as specialty gas environments or cryogenic temperatures. Examples of this method are described in reference 162.

There have been some demonstrations of 3D strain mapping using electrons. For instance in 2015, Goris et al. imaged a Au nanodecahedron using HAADF-STEM tomography [163]. By generating an atomic resolution 3D map, the 3D strain profile was determined. A similar example was shown for strain mapping on the tip of a tungsten needle [164]. However in these examples, very small structures (only $\sim 90,000$ atoms for the Au particle) were reconstructed, and this type of analysis would be very time consuming and challenging for the larger nanostructures of interest. Additionally, since these techniques image atomic planes, then convert real space lattice spacing to strain (instead of imaging in reciprocal space) the strain precision is limited ($\sim 0.1\%$). Ultimately, strain mapping using electron microscopy is limited to very small samples, as the large absorption cross-section of electrons means that the likelihood of multiple scattering in a thick sample is high, preventing analysis of elastic scattering necessary for strain measurements.

2.3.6. Summary and limitations: electron microscopy

Electron microscopy is a versatile and highly useful technique for imaging crystalline structure, morphology, and composition in nanostructures. It is complementary to atom probe and X-ray imaging and will be used as such in this work. However, there are many limitations that prevent electron microscopy from being used as the primary strain/structure tomography method in this thesis. First, electron microscopy is limited in field of view, as it takes significant time to produce high resolution (especially 3D) images. The strain precision of electrons is about an order of magnitude lower than that of X-rays, $\sim 0.1\%$ compared to $\sim 0.01\%$ using high-intensity X-rays. Electrons interact more strongly with matter than X-rays, meaning the chance of beam damage is higher. TEM/STEM also have stringent sample cleanliness requirements, particularly for high resolution imaging. Plasma cleaning or ion milling is most often required for removal of carbon contamination. These cleaning processes can often damage sensitive materials, such as InGaAs. Finally, electron microscopy is limited to thin samples especially for high resolution imaging. Many of the nanowires investigated here are >100 nm in diameter. This means that cross-sectioning or milling is required for analysis. While this does not completely rule out use of electron microscopy, milling can potentially modify the strain state in nanowires and can prevent correlation with atom probe, another destructive technique.

2.4. Characterization of Strain and Structure using Synchrotron X-rays

This section reviews three synchrotron-based X-ray techniques used in this thesis: Bragg coherent diffraction imaging, Bragg ptychography, and nano-probe diffraction. These techniques allow for high-resolution strain imaging in nanostructures. In particular, hard X-rays (energy >5 keV) are penetrating and can therefore probe strain at buried interfaces without the need for milling or cross-sectioning of the sample. As such, X-ray imaging is complementary to atom probe tomography, electron microscopy, and other destructive techniques. Two coherent diffraction X-ray imaging techniques, BCDI and Bragg ptychography (for imaging extended objects), are used in this work to image 3D strain and structure in nanowires. Nano-diffraction is used to map variations in strain, in projection, in single nanowires. BCDI and Bragg ptychography provide higher spatial resolution than typical X-ray measurements thanks to the use of high brightness synchrotron sources, advanced X-ray optics, and phase retrieval algorithms (in the case of coherent diffraction). Measurements in this thesis were performed at the 34-ID-C beamline of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) for BCDI, the 3-ID Hard X-ray Nanoprobe (HXN) of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL) for Bragg ptychography, and at the 26-ID-C Nanoprobe of APS for nano-diffraction.

2.4.1. Introduction to X-ray diffraction of nanocrystals

2.4.1.1. X-ray fundamentals. A new form of ionizing electromagnetic radiation, X-rays, was discovered in 1895 by Wilhelm Röntgen. X-rays were found to be highly penetrating in nature, which was later determined to be due to their refractive index being close to unity. This observation led to X-rays being used broadly for imaging internal structure, such as in medical imaging or imaging for security (for example in airports). In 1912 the first ever diffraction from a crystal was recorded by the von Laue group, which was possible because the spacing between atomic planes (~ 1 Å) and the wavelength of X-rays (0.01-10 Å) are within the same Ångstrom range [165, 166]. The theory of Bragg X-ray diffraction from crystals was developed by W. H. Bragg within a year of the first X-ray measurements [167, 168].

During diffraction, an X-ray beam traveling along an incident wave vector k_i is scattered from a crystal. The final wave vector k_f defines the direction in which constructive interference of these scattered waves occurs; along k_f measurable signal is expected. The determination of whether constructive interference will occur to produce diffraction is given by Bragg's Law:

$$(2.1) \quad 2d \sin(\theta) = n\lambda$$

where d is the spacing between a crystals lattice planes, 2θ is the angle between the incident and final wave vectors (k_i, k_f) , and λ is the wavelength of the incident X-rays. The vectorial description of this scattering is given by:

$$(2.2) \quad \vec{q} = \vec{k}_i - \vec{k}_f$$

where $\vec{q}$ is the momentum transfer given by:

$$(2.3) \quad |\vec{q}| = \frac{2\pi}{d}$$

This equation describes the Fourier relationship between real space periodicity d and the momentum transfer $\vec{q}$. The impact of this is that periodicity in real space, whether an interplanar spacing or some other larger reoccurring feature (such as a periodic layered structure), will be encoded as an inverse magnitude in reciprocal space.

The spacing between atomic planes along a particular $[hkl]$ miller direction in a simple cubic crystal is:

$$(2.4) \quad d_{hkl} = \frac{a}{h^2 + k^2 + l^2}$$

where a is the lattice spacing of the crystal. This d-spacing d_{hkl} is used to described the periodicity in real space which yields Bragg scattering at the (hkl) condition. The calculation of d_{hkl} is different for the different crystal symmetries, but can be found in literature [96]. For scattering from (hkl) planes, Bragg's law is fulfilled when the momentum transfer vector $\vec{q}$ coincides with the Bravais reciprocal lattice vector $\vec{G}_{hkl}$, as described by Laue's law:

$$(2.5) \quad |\vec{q}| = |\vec{G}_{hkl}| = \frac{2\pi}{d_{hkl}}$$

The Bravais reciprocal lattice in Equation 2.5 is given by:

$$(2.6) \quad \vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$

and the corresponding Bravais real space lattice vector is given by:

$$(2.7) \quad \vec{R}_m = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$$

where $\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*$ are reciprocal lattice vectors and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the corresponding real space unit cell vectors where $m_{1,2,3}$ are the m^{th} unit cell in each of the three dimensions. The atomic positions of any given atom can be defined then as:

$$(2.8) \quad \vec{r}_n = \vec{d}_n + \vec{R}_m$$

where d_n is the offset of this atom in its unit cell. [169, 170]

2.4.1.2. X-ray scattering from crystals. The scattering amplitude and phase of a particular crystal is defined by two features: the crystal shape and the crystal structure factor (F). First, the crystal shape or crystal form factor for a crystal of $N_1 \times N_2 \times N_3$ unit cells is given by:

$$(2.9) \quad L(\vec{G}_{hkl}) = L_{hkl} = \sum_{m_j}^{N_j} e^{2\pi i \vec{G} \cdot \vec{R}_m}$$

Second, the structure factor accounts for the amplitude due to X-ray interactions with specific atoms (defined by their atomic form factor, f_n) and the lattice symmetries in the crystal. The structure factor is calculated by summing all the amplitudes of single atoms in the crystal, but is simplified due to symmetry as follows:

$$(2.10) \quad F(\vec{G}_{hkl}) = F_{hkl} = \sum_n f_n e^{2\pi i \vec{G}_{hkl} \cdot \vec{r}_n}$$

Finally, the complex scattering of the crystal is the combination of Equation 2.9 and 2.10:

$$(2.11) \quad \hat{\psi}_{hkl} = L_{hkl} F_{hkl}$$

This is sometimes referred to as the electron density $\rho(\vec{r})$ of the crystal. The intensity recorded during diffraction is the absolute square of $\hat{\psi}_{hkl}$:

$$(2.12) \quad I_{hkl} = |\hat{\psi}_{hkl}|^2$$

When a crystal is large the crystal form factor converges to a delta function, $L_{hkl} \xrightarrow{N_j \rightarrow \infty} \delta_{hkl}$, so scattering intensity will only be seen at the exact $\vec{q} = \vec{G}_{hkl}$ condition. This is why diffraction of homogeneous bulk crystals results in scattering at narrow angular conditions, and in the limit of a perfect crystal the diffraction would occur as delta functions around the $\vec{G}_{hkl}$ reciprocal lattice points. However, for nanocrystals, such as the nanowires in this work, L_{hkl} results in a broadening of $\vec{q}$ values at which

scattering is observed. Specifically, the crystal form factor defines the full width half maximum (FWHM) of the scattering in $\vec{q}$ to be inversely proportional to the crystal size, known as the Scherrer effect [171]. Thus, diffraction from nanocrystals produces 3D intensity patterns defined by the nanocrystal dimensions and structure factor. [172, 173, 174]

2.4.1.3. Strain and structure mapping in nanocrystals using X-rays. For a given crystal, the crystal form factor is fixed, so variations in ψ_{hkl} within the crystal are defined by the structure factor. The structure factor accounts for changes in crystal phase (structure) and deviations in atomic planes from the ideal d_{hkl} spacing (resulting from strain or defects). For the polytypic nanowires investigated in this work, the structure factor is calculated to determine how ψ_{hkl} will change in amplitude and phase due to changes in crystal phase. Further, the structure factor is calculated to determine at what (hkl) conditions diffraction is forbidden ($I_{hkl} = 0$), known as selection rules. For WZ III-V crystals, the structure factor is given by:

$$(2.13) \quad F_{hkl}^{WZ} = (f_{\text{III}} + f_{\text{V}} e^{-i\pi \frac{3l}{4}}) (1 + e^{-i\pi \frac{2h+4k+3l}{3}})$$

and for ZB:

$$(2.14) \quad F_{hkl}^{ZB} = (f_{\text{III}} + f_{\text{V}} e^{-i\pi \frac{h+k+l}{2}}) (1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)})$$

where f_{III} and f_{V} are the atomic form factors for the group-III and group-V species [175, 176]. Since the scattering intensity is proportional to the complex conjugate of the structure factor ($I_{hkl} \propto |F_{hkl}|^2$ from Eqns 2.11 and 2.12), the (hkl) values where diffraction is zero and non-zero can be determined (selection rules). For ZB, diffraction occurs when h,k,l are all odd or when h,k,l are all even. WZ diffraction is allowed when $2h + 4k + 3l = 3p$, where p is an integer. It is important to note that the h,k,l indices for WZ are the 3-index abbreviation of the 4-index miller notation (hkil), which are not equivalent to the h,k,l values used for ZB [177]. These selection rules are useful because there exist (hkl) conditions where ZB is allowed and WZ is disallowed, and visa versa. There are also conditions where ZB and WZ are both allowed or disallowed. Thus, (hkl) conditions can be selected to probe polytypism in III-As nanowires. Beyond the selection rules, structure factor calculations can be used to determine the phases of different stacking orders of WZ or ZB crystals, which is discussed in Chapter 4.

Since the structure factor is the sum of all unit cells in the crystal, treatment of imperfect crystals requires the addition of a term to Equation 2.10 to account for deviations from the known Bravais lattice positions $\vec{R}_n$:

$$(2.15) \quad \vec{F}_{hkl} = \sum_n f_n e^{2\pi i \vec{G}_{hkl} \cdot \vec{r}_n} e^{2\pi i \vec{G}_{hkl} \cdot \vec{u}_{hkl}}$$

where $\vec{u}_{hkl}$ is the displacement of the unit cell with respect to the expected $\vec{R}_m$ lattice position. The strain on the reference lattice along the specified [hkl] direction is related to the displacement by:

$$(2.16) \quad \epsilon_{hkl} = \frac{\delta \vec{u}_{hkl}}{\delta x_{hkl}}$$

Therefore the scattering amplitude of a nanocrystal for the (hkl) condition is given by:

$$(2.17) \quad \hat{\psi}_{hkl} = L_{hkl} \sum_n f_n e^{2\pi i \vec{G}_{hkl} \cdot \vec{r}_n} e^{2\pi i \vec{G}_{hkl} \cdot \vec{u}_{hkl}}$$

If a nanocrystal consists of a single Bravais lattice $\vec{G}_{hkl}$ (no structure change), the displacements ($\vec{u}_{hkl}$) can be related to variations in the scattered phase (ϕ) by:

$$(2.18) \quad \hat{\psi}_{hkl} = \hat{\psi}_0 e^{i\phi}, \text{ where } \phi = 2\pi \vec{G}_{hkl} \cdot \vec{u}_{hkl}$$

Here ψ_0 is the scattering amplitude of the unstrained portion of the crystal. However, since x-ray detectors only measure intensity (Eqn. 2.12), the phase information relating to the displacement field is lost. This is known as the “phase problem” and will be discussed further in Section 2.4.2 [178].

2.4.1.4. Synchrotron X-ray sources. Three types of X-ray sources are used for materials characterization: X-ray laboratory sources, synchrotrons, and X-ray free electron lasers (FELs). X-ray lab sources use either X-ray tubes or anodes, to generate X-rays by bombarding a metal target with accelerated electrons to produce X-ray fluorescence [172]. Synchrotrons and FELs produce X-ray radiation of much higher brilliance by bending relativistic electron beams [179]. Brilliance (or brightness) is a measure of X-ray flux (number of photons/second/area in a 0.1% bandwidth (BW)) that accounts for the angular distribution of the beam, and is measured in units of *photons/(sec · mm² · mrad² · 0.1%BW)*. In both synchrotrons and FELs, RF or pulsed DC electron guns are used to inject electrons into a linear accelerator (LINAC). LINACs consist of a series of RF resonant cavities, which accelerate electrons to relativistic speeds and drives them into bunches of defined wavelength. From there, FELs transversely bend the electrons using periodic structures of dipole magnets, called undulators. This bending results in generation of X-rays, using ~1% of the electron beam energy; the remainder of the beam is decelerated

and sent into a beam dump [180, 181]. In synchrotrons, after traveling through the LINAC, relativistic electrons are injected into a low pressure circular storage ring that maintains the electron beam focus and energy. A LINAC is used to periodically top off the electron beam in the storage ring to make up for the energy lost to X-ray production. At discrete curves in the storage rings, bending magnets are used to curve the electron beam to maintain a circular path. Between the bending magnets, an insertion device (ID), which is another type of undulator, is used to periodically perturb the electron beam to generate a high brightness photon source at a specified energy that is determined by the spacing between individual magnets in the undulator [182, 174].

The metrics of interest when choosing an X-ray source for a particular experiment include brilliance, source focusing (which depends on source size and angular divergence), wavelength, time-resolution, and coherence. The specific experiment establishes the priority of these needs. While lab sources are broadly available and easier to use, many experiments require the characteristics of synchrotrons or FELs. An overview of the different properties of interest is shown in Table 2.1 [174]. FELs are extremely useful for low signal measurements (due to its higher brilliance) and for measurements that require extremely high time-resolution. Additionally, FELs offer very long coherence lengths. However, only a 1-2 experimental end-stations are available for use at FELs simultaneously, compared to 30+ end-stations at synchrotrons. Synchrotrons therefore offer a higher degree of flexibility in terms of end-station equipment and user access. In this work, synchrotrons are used as the X-ray sources for the coherent X-ray imaging and nano-probe X-ray diffraction experiments discussed in Sections 2.4.2 - 2.4.4. The moderate coherence lengths and potential for nano-focusing make synchrotrons suitable for these types of experiments.

In 2016, the MAX-IV light source in Sweden became the first synchrotron to be upgraded to a diffraction limited storage ring (DLSR), otherwise known as a 4th generation synchrotron. In 2020, the European Synchrotron Radiation facility (ESRF) in France completed the same upgrade, and an upgrade of the Advanced Photon Source in the US is planned for 2022. DLSRs use multi-bend achromat magnets to bend the electron beam more gradually around the storage ring than traditional bending magnets. This allows the electron beam to maintain a very low emittance, which controls the average brightness and the coherent fraction of the beam. The average coherence lengths improve from 10-100 μm in 3rd

Table 2.1. Comparison between properties of different sources. Adapted with permission from reference 174. Copyright © 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

Source	Tubes	Synchrotrons	FELs
Size-typical	few mm	few 100 μm	few mm
Size-focus	70 μm	0.05 μm	N/A
Wavelength	Fixed (target)	Extremely flexible	Flexible
Divergence	2-20°	1-100 μrad	< 100 μrad
Brilliance	10 ⁷ -10 ⁹	10 ¹⁷ -10 ²⁰	10 ²³ -10 ²⁵
Time-resolution	no intrinsic	100 ps in timing mode	fs
Transverse Coherence	nm	10-100 μm	0.1-10 mm

generation sources to 1-10 mm in DLSRs. As such, DLSRs will enable major advances in the field of Coherent x-ray imaging [183, 184].

2.4.1.5. X-ray focusing. Section 1.4.5 motivates investigation of composition, crystal phase, and strain at the nanoscale using highly-spatially resolved characterization techniques like atom probe tomography and electron imaging. Electron imaging is a useful high resolution tool for strain characterization as discussed in Section 2.3.3. HAADF-STEM can map strain down to 1 nm spatial resolution, and nano-beam precession electron diffraction can achieve strain resolutions of 0.05% with a few nanometer spatial resolution. However, these high resolution imaging techniques require thin samples (<100 nm) and cannot match the strain resolution provided by X-rays (<0.01%). As such, the ability to focus X-rays to selectively image nanostructures is of great interest. However, X-rays are much more difficult to focus than optical photons because their refractive index, given by:

$$(2.19) \quad n = 1 - \delta + i\beta$$

approaches unity in common optics materials. In particular, the hard X-rays used for materials science have a very low refractive decrement δ (real part of the refractive index). Normalized by material density, $\delta/\rho < 10^{-5} \text{ cm}^2/\text{g}$ for all elements (for X-ray $E > 6 \text{ keV}$) as compared to that of visible light in glass, for which $\delta/\rho \sim -0.2 \text{ cm}^2/\text{g}$ [185]. A small decrement δ means that the angle of refraction through a medium is small, so X-rays are very difficult to bend. The imaginary component in Eqn 2.19, which determines the mass-absorption of X-rays, is between 10^{-7} - 10^{-8} in most materials (but increases strongly with atomic number), indicating the highly transmissive nature of X-rays. There are many resources available for

the calculation of absorption and refraction properties of X-rays in pure and compound materials in the literature [186, 187].

Despite the very low refractive decrement, refractive optics have been designed. Compound refractive lenses (CRLs) use a linear array of refractive lenses to consecutively bend the X-rays into focus. Since X-rays must travel through many lenses, materials of low atomic number, such as Li, B, Be, and C materials and compounds, are used to prevent attenuation [188]. X-rays can also be focused with reflective and diffractive optics. The most common reflective optic is the Kirkpatrick-Baez (KB) mirror, which uses total external reflection or multilayer reflection via ultra-low roughness elliptical mirrors, typically with metal coatings, to achieve highly focused hard X-ray beams with minimal loss of brilliance [189, 190]. Capillary optics have also been used to focus X-rays using total external reflection but are limited to micron beam waists.

Diffractive optics use a lattice of alternating low and high density materials to diffract X-rays to a focal point. The most common diffractive optic, and the optic used throughout this thesis, is the Fresnel Zone Plate (ZP). ZPs consist of circular gratings that alternate between transparent and opaque rings. The grating, or zone structure, decreases in periodicity towards the outside of the ring as shown in Figure 2.4(a). The properties of zone plates are primarily defined by the X-ray wavelength, the width of the outermost zone (Δr) and the number of zones (N). The focus resolution of a perfect ZP is given by:

$$(2.20) \quad \text{Resolution} = 1.22 \frac{\lambda}{2NA} = 1.22 \Delta r_n$$

where NA is the numerical aperture:

$$(2.21) \quad NA = \frac{\lambda}{2\Delta r}$$

The focal length f is given by:

$$(2.22) \quad f = \frac{4N(\Delta r^2)}{\lambda}$$

and the depth of focus DoF is given by:

$$(2.23) \quad DoF = \pm \frac{\lambda}{2(NA^2)}$$

These equations are used to estimate the beam spot size and determine the approximate focal plane, at which the sample is placed [191, 174, 192] [193]. ZPs focus X-rays with about 10% efficiency, with the other 90% lost to absorption or higher order diffraction. Thus the high brilliance of synchrotron sources

is required to produce a focused probe with sufficient flux for X-ray experiments. For focusing of high energy X-rays, the long attenuation length requires the opaque rings in ZPs to be microns in height even for dense metals. Since ZP resolution is dependent on the width of the outermost zone, Δr must be very small for nano-focused beams. However, fabrication of ZP optics with such high aspect ratios is very challenging, and currently limit Δr to around 20 nm. Therefore, other approaches to forming ZPs have been developed, such as zone plate doubling, which involves precisely stacking zone plates of lower aspect ratio to achieve higher effective aspect ratio zones. Alternatively, multilayer Laue lenses (MLLs) have been developed that flip this fabrication process on its side. Instead of etching high aspect ratio metal layers for a ZP, MLLs use monolayer precision magnetron sputtering to grow multilayer films which are then thinned laterally to create extremely high aspect ratio zones. MLLs focus X-rays into 2D lines, so two MLLs rotated 90° from one another produce a 3D focused spot, as illustrated in Figure 2.4(b) [194]. ZPs and MLLs have been used to achieve X-ray beams focused down to 7.8 nm² for ZPs [195] and 8.4×6.8 nm² for MLLs [196].

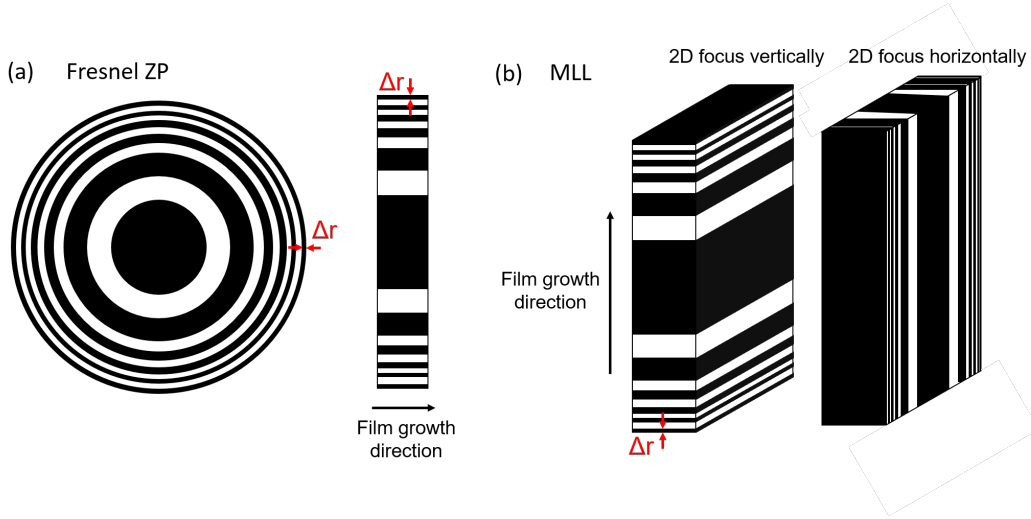


Figure 2.4. Schematic Fresnel zone plate and multilayer Laue lens (a) ZP from front view and side view. Δr defines the maximum resolution of the focus. Large aspect ratios in fabrication are hard to achieve, limiting ZP resolution. (b) Two MLLs used to focus beam into a 3D spot. The film growth direction is opposite to the ZP creating very thin layers by magnetron sputtering, allowing for high aspect ratio zones.

Recent advances in the field of X-ray optics have enabled nano-scale imaging with X-rays at dozens of beamlines around the world. Regular use of ~ 100 nm probes is possible, as well as semi-regular use of 15-25 nm probes. While X-rays are still very far from achieving the sub-nm focuses offered by electron imaging, they are approaching the same spatial resolution available for electron microscopy-based strain mapping. Additional approaches to achieve spatial resolution beyond the X-ray spot size are discussed in Section 2.4.2 and 2.4.3.1.

2.4.2. Coherent X-ray diffractive imaging

2.4.2.1. Introduction to coherent scattering in crystals. Coherence refers to the alignment of temporal and spatial phase in electromagnetic waves. Temporal coherence refers to the degree of alignment in longitudinal phase, which corresponds to the monochromaticity of a beam. Spatial coherence refers to the degree of alignment in the transverse phases of the wave. Synchrotrons are not intrinsically sources of coherent radiation, but if the brilliance is high, as in 3rd generation synchrotron sources ($> 10^{18}$ photons/(s $\cdot$ mm² $\cdot$ mrad² $\cdot$ 0.1%BW)), a combination of pinholes and monochromators can be used to extract a sufficiently bright and coherent beam. The lateral width of the spatially coherent portion of an X-ray beam impinging on a sample can generally be described by the wavelength and the sample distance (D) away from the source according to:

$$(2.24) \quad L_t = \frac{\lambda D}{2\sigma_r}$$

where $2\sigma_r$ is the width of the coherent beam at the source (typically several hundred microns for 3rd generation synchrotrons). Given the distance dependence, most coherent beamlines are built 50-100 m away from the insertion device. This results in lateral coherence lengths on the order of a few μm and vertical coherence lengths on the order of a few tens of μm for hard X-rays. DLSRs have source sizes that are diffraction limited so σ_r is

$$(2.25) \quad \sigma_r = \frac{\sqrt{R\lambda}}{4\pi}$$

Where R is the length of the insertion device (typically a few meters). This means at a DLSR, a 50 m beamline with a 4 m insertion device at 12 keV will have transverse coherence at the sample as large as 160 μm . However, at both 3rd generation and DLSR synchrotrons there can be additional sources of

coherence length reduction between the insertion device and the sample [197]. Thus coherence lengths are often limited to $\sim 2\text{-}3\text{ }\mu\text{m}$ at some 3rd generation coherent beamlines [198].

These coherence lengths define the spatial region in which the complex amplitude ψ of the photons far from the source have the same phase ϕ . When a coherent X-ray beam impinges on a sample, the waves scattered from the sample will interfere and produce fringed intensity patterns on a detector. If the sample is fully illuminated by a coherent x-ray beam (*i.e.* the sample is smaller than the transverse coherence length) then the interference patterns will encode information about the sample electron density ρ . The electron density ρ describes any effects that lead to Thompson scattering, which includes the sample shape and density. If a crystalline sample is a Bragg geometry, then ρ includes strain effects as described by Eqns. 2.11 and 2.17. In the near field (close to the sample) the diffracted amplitude has a spherical wavefront, but at a distance Z far away from the sample ($Z \gg a^2/\lambda$, where a is the sample size), the wavefront is approximately flat (Fraunhofer approximation). Thus the scattering amplitude for a given momentum transfer ($\vec{q}$) can be approximated as:

$$(2.26) \quad \hat{\psi}(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r}$$

where $\vec{r}$ is the position within the sample. Therefore the complex scattering in the Fraunhofer regime is simply the Fourier transform ($\mathcal{F}$) of the complex electron density of the illuminated object:

$$(2.27) \quad \hat{\psi}(\vec{q}) = \mathcal{F}\rho(\vec{r})$$

If the scattered wavefield is collected in the vicinity of a Bragg reflection ($\vec{G}_{hkl}$), the deviations in strain encoded in the scattering amplitude can be written as:

$$(2.28) \quad \hat{\psi}(\vec{q}) = \mathcal{F}\rho'(\vec{r}) e^{i\vec{G}_{hkl} \cdot \vec{u}(\vec{r})}$$

where $\rho'(\vec{r})$ is the electron density of the perfect crystal. As such, scattering of coherent X-rays is sensitive to 3D strain fields, motivating their use for strain imaging [182, 199, 200, 184, 174]. However, as discussed in Section 2.4.1.2, X-ray detectors cannot record electromagnetic phase, only the intensity (Eqn. 2.12). Therefore, a simple inverse Fourier transform of the intensity pattern will not reproduce the crystal density as would be the case if both amplitude and phase were collected. This is known as the “phase problem”.

2.4.2.2. Lens-less imaging and the phase problem. In lens based microscopy, the scattered beam collected from the sample is magnified by a lens to produce an image of the object. This is the method employed in most optical and electron imaging, and the resolution is typically limited by the chromatic aberrations of the lenses. However, as discussed previously, refractive X-rays optics are very inefficient, so defocusing the diffracted beam would not yield enough signal to image the sample. Instead, approaches that retrieve real space crystal information without the use of lenses are required. These “lens-less” imaging techniques use an algorithm known as “phase retrieval” in place of an objective lens to convert reciprocal space intensity patterns into a real space image [201, 200]. The resolution is no longer limited by the lens aberrations, but by the resolution of information collected in reciprocal space. Coherent diffraction imaging (CDI) is a form of lens-less X-ray imaging used to probe the crystal density function ρ . Bragg coherent diffraction imaging (BCDI) refers to lens-less X-ray imaging performed at a Bragg peak, at which point ρ encodes information about crystal strain fields.

Phase retrieval is usually implemented using an iterative algorithm developed by Gerchberg and Saxton. One makes an initial guess of the complex wave field $\hat{\psi}$ and iterates back and forth between real and reciprocal space using a series of fast Fourier transforms (FFT). At each iteration, the absolute square of the guessed wavefunction $\hat{\psi}$ is compared to the measured intensity patterns until the difference is minimized. The typical process flow for CDI is described in Figure 2.5. Here the real space steps are boxed in blue and reciprocal space steps are boxed in black. Red arrows denote constraints, and black arrows denote FFT or FFT^{-1} . The general process starts by defining a starting guess for the real space image ρ_1 ; the guess consists of a real space support S of amplitude 1 and random phase values ϕ_1 . An FFT converts this to the reciprocal space wave function $\psi_n = |\psi_n| \cdot e^{i\Phi_n}$ with amplitude $|\psi_n|$ and phase Φ_n , where $n=1$ on the first iteration. The amplitudes, $|\psi_n|$, are then replaced by the square root of the measured intensity values. Then an FFT^{-1} converts ψ_n back into real space, giving a new ρ_n with amplitude values $|E_n|$ and phase values ϕ_n . The real space constraint S is again applied, replacing the amplitudes in ρ_n and starting a new iteration, $n+1$. This process is repeated for N iterations until the solution ρ_n is reached. Many mathematical approaches have been taken to find the best solution (global

minimum) in the phase retrieval process. Common algorithms include Error Reduction, Hybrid Input-Output, difference mapping, maximum likelihood, and Solvent Flipping. Details on these algorithms can be found in literature [202, 203]. Originally, the support requirement in CDI required knowledge of the sample shape and size. However, the development of a “shrinkwrap” method allows for the support to be modified during each iteration, gradually constraining more and more of real space until the object shape has been reproduced [201].

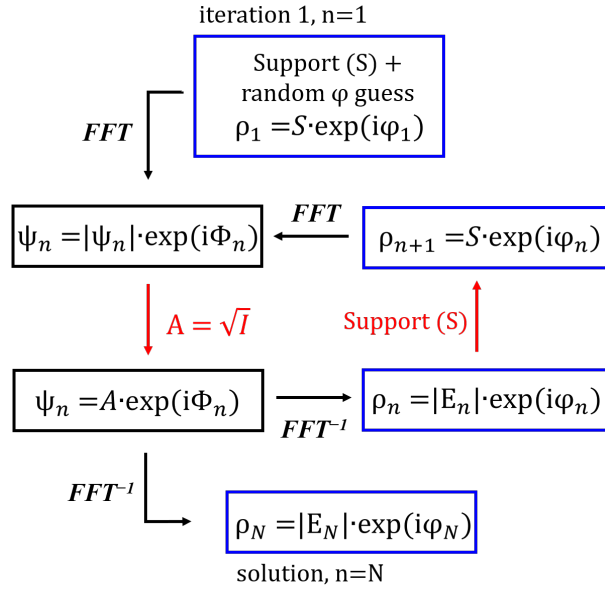


Figure 2.5. Typical process flow for phase retrieval in CDI. Real space and reciprocal space steps are shown as blue and black boxes respectively. Red arrows denote application of constraints. Black arrows represent fast (inverse) Fourier transforms.

The outcome of a coherent diffraction imaging measurement can be described as a weighting of constraints and unknowns. If the unknowns outweigh the constraints, then a solution is not possible. Therefore, the existence of a single solution to this minimization problem relies on the oversampling of diffracted intensities [204]. The Nyquist-Shannon sampling theorem states that for phase retrieval to converge, the reciprocal space pattern must be oversampled by a factor of two. For an intensity pattern measured at the detector, the individual interference fringes should be sampled by at least two detector pixels. Additionally, in real space, the sampling range must be twice the object size; this constrains

the phase retrieval in real space since at least 50% of the real space image will produce an amplitude and phase of zero. Oversampling beyond the Nyquist frequency will allow for faster convergence of the phase retrieval algorithm. The oversampling rate must be balanced with the signal-to-noise ratio in the detector. Moving the detector further away from the sample allows for larger oversampling, but if it is too far, the signal-to-noise on the detector will be too low to measure intensity from weak interference fringes (due to X-ray air scattering). The choice in detector position will be mandated by the intensity of the scattered diffraction, the real-space resolution desired, and the constraints of the beamline [201, 205].

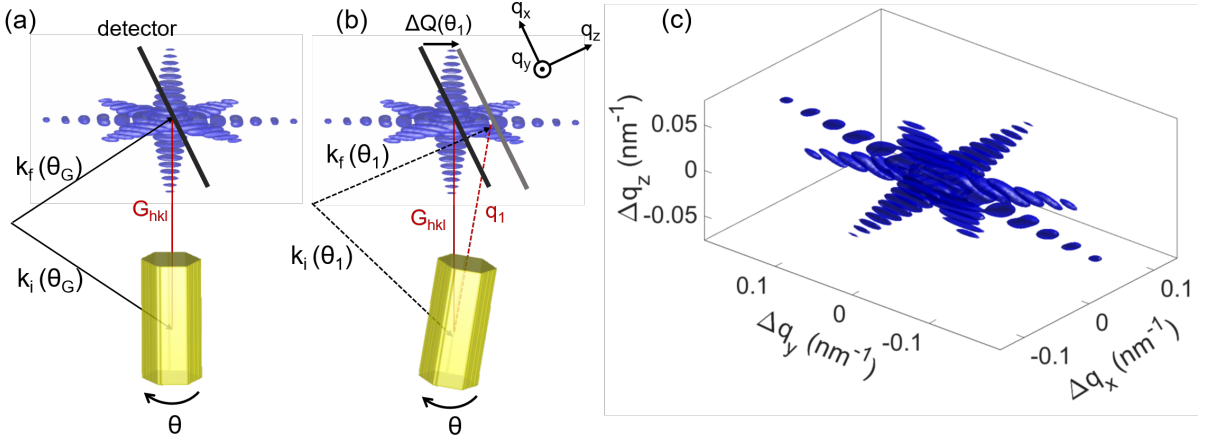


Figure 2.6. Schematic of BCDI experiment. A nanorod (yellow) and its corresponding 3D Bragg peak (blue). (a) Intensity sampling using a 2D detector maps the Bragg peak at its center position (θ_G) in q_x and q_y . (b) The third reciprocal space dimension q_z is probed by rocking the nanorod to a new angle θ_1 . The momentum transfer $\vec{q}_1$ no longer matches the Bragg condition $\vec{G}_{hkl}$, deviating in reciprocal space by the vector $\Delta\vec{Q}(\theta_1)$. Without moving the detector, a new slice of the Bragg peak is recorded. Rocking in fine angular steps over θ records all three reciprocal space dimensions (labeled as q_x , q_y , and q_z). (c) A 3D reciprocal space map (RSM) of the Bragg peak intensity.

2.4.2.3. BCDI measurements. The CDI measurements performed in this thesis are done in the Bragg geometry (BCDI) in order to probe strain in nanowires. For BCDI measurements, X-ray beams are usually focused to a few microns, since the coherence lengths at the sample are typically around 2-3 μm . An isolated nanocrystal is placed under the X-ray beam at the Bragg condition (hkl). The nanocrystal must fit fully within the coherent portion of the beam, otherwise phase retrieval is not possible (a real space support S does not exist). A schematic of a BCDI measurement on a nanorod is shown in Figure 2.6. The

sample is rotated with respect to the incident beam $\vec{k}_i$ such that the momentum vector $\vec{q}$ aligns with the Bravais lattice vector $\vec{G}_{hkl}$ (the Bragg condition is fulfilled), as shown in 2.6(a). As discussed in Section 2.4.1.2, the finite dimensions of a nanocrystal results in a broadening of the Bravais reciprocal lattice point (Bragg peak). Thus a 3D sampling of intensity is required to image the Bragg peak. A charge coupled device (CCD) detector is rotated to the known angular location of the exit wave k_f , at a typical distance of 0.5 - 1 m from the sample plane. A diffraction intensity pattern is recorded on the detector in 2D, accessing two reciprocal space dimensions q_x and q_y . To access the third dimension q_z , the sample is rocked in fine angular steps ($\sim 0.1^\circ$) over the entire Bragg peak. This collection of measurements over a range of angles is referred to as a rocking curve, as shown schematically in 2.6(b), for which the nanorod is rocked in θ to a new angle θ_I (off angle to the Bragg condition $\vec{G}_{hkl}$ which is at angle θ_G). This new momentum vector $\vec{q}_I$ is offset from $\vec{G}_{hkl}$ by $\Delta\vec{Q}(\theta_I)$. Rocking the angle of the sample probes $\vec{q}$ for small deviations from the Bragg condition ($\vec{G}_{hkl}$):

$$(2.29) \quad \vec{Q} = \vec{q} - \vec{G}_{hkl}$$

$\vec{Q}$ here describes the vectorial change in reciprocal space due to the angular deviation away from the Bragg condition [206, 207]. The detector remains fixed, but a different cut of the Bragg peak is imaged due to the angle change. This same effect can also be achieved without rotating the sample by tuning the wavelength of the incident X-ray beam [206], which is useful for sample environments that constrict motion such as during *in situ* or *in operando* experiments. The reciprocal space dimensions probed during a BCDI measurement are shown with respect to the detector orientation in 2.6(b). Figure 2.6(c) shows a simulated 3D reciprocal space map (RSM) of the nanorod's Bragg peak at the (hkl)=(111) condition. The crystal truncation rods expand in 8 dimensions due to the faceting of the nanocrystal (6 for the hexagonal facets, 2 for the top and bottom facets). These fringes must be oversampled by a factor of at least 2 to allow for phase retrieval, discussed in Section 2.4.2.2. The oversampling requirement can also be expressed in terms of the minimum rotation angle $\Delta\theta$ and the subtended angle ($\Delta\gamma$) of each detector pixel:

$$(2.30) \quad \Delta\theta, \Delta\gamma < \frac{\lambda}{2a}$$

where a is the dimension of the lateral object. The subtended angle is the angular range detected across a single pixel (in both x and y) and is given by:

$$(2.31) \quad \Delta\gamma = \arctan \frac{s_p}{D}$$

Where D is the detector - sample distance and s_p is the detector pixel size (55 μm for the detectors used in this work). As mentioned previously, the real space resolution is not limited by the probe size, but instead by the resolution of information recorded in reciprocal space. The real space resolution is given by:

$$(2.32) \quad \text{Resolution}_{x,y,z} = \frac{D\lambda}{\Delta q_{x,y,z} s_p}$$

where $\Delta q_{x,y,z}$ is the extent of scattering in each reciprocal space dimension $\vec{q}$. Note that the spatial resolution is often asymmetric due to differences in scattering intensities in each direction.

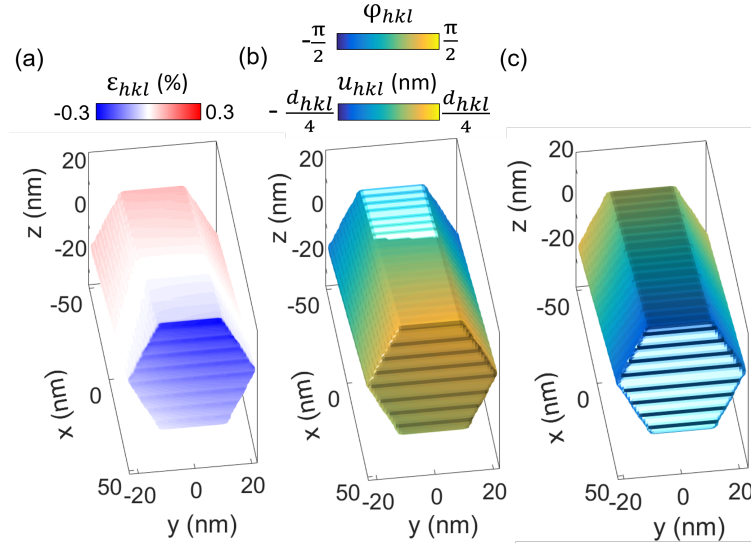


Figure 2.7. Example of CDI reconstruction post-processing requirements. (a) Strain field along the (hkl) planes of a nanorod (ϵ_{hkl}). White regions denote the unstrained crystal lattice. CDI measurements performed on the nanorod will produce a phase map (b). Phase is converted to lattice displacement with respect to the unstrained lattice (d_{hkl}) according to Eqn. 2.18. Then displacement is converted to strain according to Eqn. 2.16. (c) The degenerate solution $\psi^*(-r)$ to the phase retrieval problem may be reconstructed and knowledge about the scattering geometry is used to choose the correct solution ($\psi(r)$ in b).

As the phase retrieval process does not automatically produce interpretable real space images, post-processing is required, as illustrated in the example of a simulated nanorod in Figure 2.7(a)) with a varying phase field along the (hkl) planes. If the nanorod is imaged with CDI at the (hkl) Bragg condition, the reconstruction will produce a solution in terms of phase, as seen in 2.7(b). The Bragg peak must be centered around zero in the reciprocal space map to prevent any phase ramps due to angular deviations $\vec{Q}$, defined in Eqn. 2.29. Centering can be done before or after the reconstruction process. Due to the finite size of pixels in the reciprocal space grid, the peak will never be perfectly centered, so reconstructions often present a smoothly varying linear phase variation, that should be ignored. Another consideration in post processing is that the solution to the phase retrieval problem is degenerate:

$$(2.33) \quad \sqrt{I} = \vec{\psi}(r) \text{ and } \sqrt{I} = \vec{\psi}^*(-r)$$

The correct solution $\vec{\psi}(r)$ is chosen by using knowledge about the real space scattering geometry, which is more difficult for samples of high symmetry. The incorrect $\vec{\psi}^*(-r)$ solution is shown in 2.7(c). Conversion from $\vec{\psi}^*(-r)$ to $\vec{\psi}(r)$ can be done simply by flipping the amplitudes and phases in all three real space directions. After removal of phase ramps and correcting for degeneracy, the displacements in the reconstructed nanorod are converted to strain according to Eqn. 2.16, assuming that all changes in phase are due to strain. Defects in crystals also modify the displacement field, so careful interpretation of the generated strain field is required, and comparison to simulations, discussed in Section 2.5.5, is often necessary.

2.4.2.4. Possibilities and limitations of BCDI. Some of the first BCDI experiments were performed in the mid to late 2000s, on Pb and Au nanoparticles [208, 209]. Since then, BCDI has been used more widely to investigate isolated nanocrystals and polycrystalline thin films. The requirement of crystallographic isolation of a BCDI specimen typically prevents investigation of thin films. However, if the orientation of grains in the thin film are sufficiently dispersed (low texture) then under a micron focused coherent beam the Bragg peaks of different crystals may be separated in reciprocal space along the Debye diffraction ring. Such an approach has been used to investigate the strain at grain interfaces [210, 211, 212]. BCDI has also enabled *in situ* and *in operando* investigation of nanostructures. For instance, Cherukara et al. used CDI to reconstruct the 3D strain field from individual grains in a Cu

thin film under tensile loading. In another example, Ulvestad et al. mapped the phase field change in individual $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode nanoparticles in an *in situ* coin cell battery. The phase fields were used to identify and map changes in single edge dislocations within the nanoparticle during battery cycling. Other groups have used CDI to determine the location and type of defects present in nanocrystals [213, 214, 215, 216]. Nanowires and nanorods have been extensively investigated using CDI, but 3D reconstructions of nanowires have been limited to out-of-plane strain fields (strain along the nanowire growth axis) [217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230]. Chapter 5 demonstrates the generation of 3D in-plane strain reconstructions in InGaAs/GaAs nanowires using BCDI.

Though BCDI is a powerful technique for imaging 3D strain at the nanoscale, it is constrained to the analysis of compact crystals ($<3\text{ }\mu\text{m}$) due to the requirement of full illumination under a coherent beam. Many nanowires are longer than typical coherence lengths at synchrotrons, and therefore no portion of the nanowire can be reconstructed using 3D BCDI. The longer transverse coherence available at DLSRs should, in theory, allow for the investigation of much larger crystals. However, in practice BCDI is often limited by the phase retrieval process. Since the full crystal is illuminated simultaneously, a single 3D diffraction peak encodes the phase information for the entire sample. As described previously, the constraints for phase retrieval must outweigh the unknowns. The fixed constraints in BCDI are one 3D intensity pattern and one real space support, so if the phase field (the unknowns) of a crystal is too complex, there will not be a single solution to the phase problem and BCDI will not yield a realistic reconstruction. Hence, it is important to perform phase retrieval on the intensity patterns multiple times with different random starting guesses to confirm that the algorithm consistently converges to the same solution, indicating that the phase problem is sufficiently constrained. For example, Davtyan et al. and Favre-Nicolin et al. report on an under-constrained BCDI phase problem: reconstruction of GaAs(P) nanowires in the presence of stacking defects. The constraints of BCDI were insufficient to reconstruct a consistent real space image in the presence of rapid changes in phase [225, 220]. Further, for nanowires with foreign or self catalysts, the complex phase field associated with the strain at this interface or the disorder in the droplet may prevent reconstruction of the nanowire strain field.

Some beamlines now provide the capability to rapidly reconstruct 3D real space images from collected intensity patterns during an experiment. However, for the majority of samples BCDI is still not a black box tool. Knowledge of the coherent scattering and phase retrieval processes, as well as modest programming skills are typically required to produce interpretable real space images of a sample. Outside of coherent X-ray imaging groups, beamline staff are usually needed to assist with data analysis and interpretation. The next section will discuss a different coherent imaging technique known as Bragg ptychography. Ptychography may be useful for imaging strain in samples that cannot be imaged using BCDI due to their extended size or rapidly varying phase features.

2.4.3. X-ray Bragg ptychography

2.4.3.1. Introduction to ptychography. Ptychography refers to a technique in which a coherent probe is rastered across a sample and measurements are taken at overlapping positions. In X-ray ptychography, an extension of coherent diffraction imaging, a nano-focused coherent X-ray probe is scanned across a sample, and a far-field diffraction pattern is recorded at each probe position. With the introduction of probe positions as a real space constraint, the sample is not required to be smaller than the coherent beam, as in the case of BCDI. Ptychography enables the measurement of extended objects or measurement of smaller regions within a larger sample. Additionally, since diffraction patterns are recorded at each probe position (with overlap between them), phase retrieval using an X-ray ptychography dataset is a much more highly constrained problem than in the case of BCDI. Ptychography can be formulated as an extension of coherent diffraction imaging by including a probe term P_r in the expression for the scattering amplitude:

$$(2.34) \quad \psi_r = \mathcal{F}P_r \cdot \rho$$

giving the ptychography equivalent to Eqn. 2.27. The probe function represents the complex wave field of the nano-focused X-ray beam, and includes aberrations introduced by the optical components. The intensity patterns recorded during ptychography sufficiently constrain the phase retrieval process such that it is possible to simultaneously reconstruct the object ρ and the probe P when scattering in the transmission geometry ($\vec{k}_i = \vec{k}_f$). However, for Bragg ptychography (BP), as in BCDI, the diffraction is

recorded in the vicinity of a Bragg peak rather than in transmission. Therefore, after conducting a BP experiment, a transmission ptychography measurement is used to solve for the probe function. A known object ρ can be used to increase the quality of the probe reconstruction, commonly a metal test pattern in the shape of a Siemens star is used [231, 232]. In addition to oversampling by twice the Nyquist frequency in reciprocal space as in BCDI, BP uses probe overlap to encode redundancy in the diffraction patterns. For ptychography oversampling in real space, twice the Nyquist frequency implies that the probe positions must overlap by 50% [233, 207].

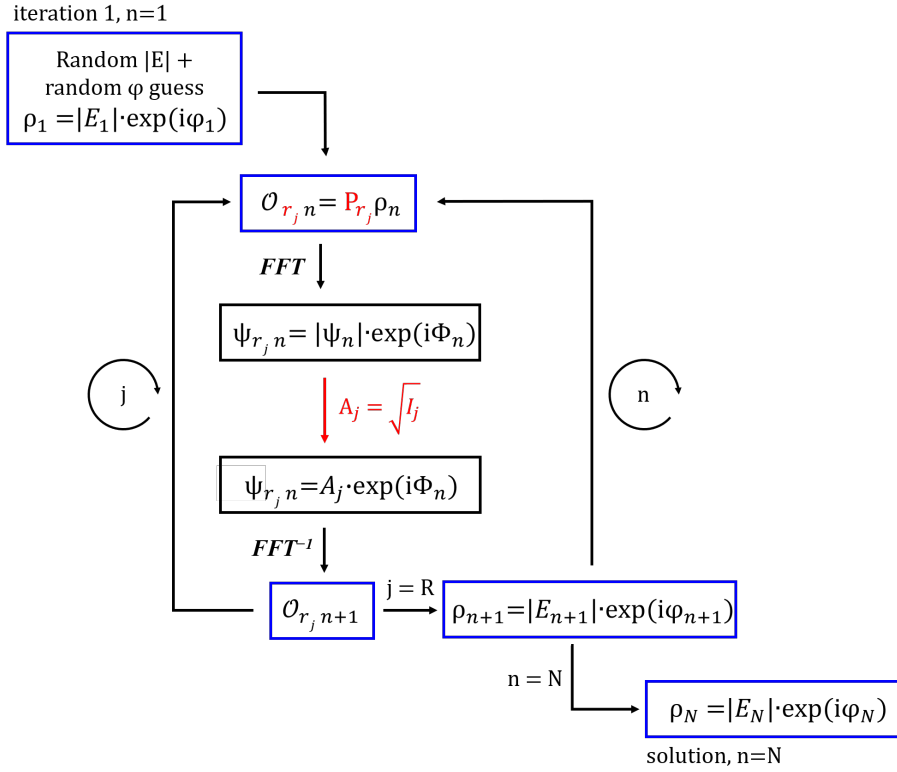


Figure 2.8. Typical process flow for phase retrieval in Bragg ptychography. Real space and reciprocal space steps are shown as blue and black boxes respectively. Red arrows or highlights denote application of constraints. FFT and FFT^{-1} denote fast (inverse) Fourier transforms.

The most common phase retrieval method for ptychography is known as the Ptychographic Iterative Engine (PIE). The general procedure for PIE is outlined in Figure 2.8. First a random guess of amplitude $|E_1|$ and phase ϕ_1 is used to define a starting crystal density ρ_1 . Next, the known probe function P_{r_j} ,

at position r_j (where $j=1$ is the first probe position) is multiplied by the guessed density ρ_1 to define a convolved real space density function $\mathcal{O}_{r_j n}$, where $n = 1$ in this first iteration. An FFT converts $\mathcal{O}_{r_j n}$ to reciprocal space, defining the scattering wave field at that probe position r_j . The scattering amplitudes are replaced by the square root of the 3D intensity pattern collected for probe position r_j , while the phases are unchanged from the starting guess. An inverse FFT converts this back to real space, giving a new amplitude and phase for $\mathcal{O}_{r_j n}$, defining new values locally (at probe position r_j) within ρ_n . This process repeats for the next probe position $j + 1$, until all the probe positions R have been used to locally update ρ_n . This updated ρ_{n+1} is then used to repeat this process for N iterations, until converging to the solution ρ_N . Numerous variations of PIE, and other algorithms, have been developed to improve phase retrieval for different types of ptychography datasets. Discussion of these methods can be found in literature [234, 235, 236].

2.4.3.2. 3D Bragg ptychography measurements. The measurement at each probe position during a 3D Bragg ptychography (3D-BP) measurement series is very similar to BCDI. The sample and detector are aligned at a Bragg condition (hkl) and a 2D intensity pattern is recorded on the detector. The sample is then rocked in small angular deviations to record slices of the 3D intensity pattern. Thus a 3D reciprocal space map of the Bragg peak is collected for a single probe position. Then the probe is moved to the next position (with 50% overlap), and the process is repeated. This process, however, is unrealistically time consuming for most samples and therefore 3D-BP has only been demonstrated a handful of times [237, 224].

There are a number of reasons why 3D-BP is so much more time consuming than BCDI. Most obviously, collecting diffraction patterns at each probe position increases the measurement time by R , if R is the number of probe positions. Given the need for 50% overlap, the number of probe positions, even for a small area, is large. For example, for a 100 nm beam, scanning a sample of $2 \times 2 \mu\text{m}$ requires at least 1600 probe positions. Beyond this, the interaction volume of a nanoprobe with a crystal is much smaller than in a BCDI experiment. This results in the need for longer exposure times to reproduce the weaker scattering tails further away in $\vec{q}$ from the Bragg peak maximum (recall that this distance defines the real space resolution of the experiment). Furthermore, an X-ray nanoprobe used in 3D-BP will provide

much lower incident flux than the micron-focused X-ray beam used in BCDI, due to the inefficiencies of X-ray optics. This also increases the exposure time needed to collect high resolution data. Another requirement of 3D-BP is that the beam location must be precisely aligned at each θ angle collected for a given position in order to generate a 3D RSM at each probe position. Both the need for long exposures at the tails of the Bragg peak and the need for exact positional alignment at every angle prevent the use of fast scanning techniques that have been developed for transmission ptychography [238]. Ultimately, the combination of all these requirements results in impractically long experimental times for most samples (many days). An alternative measurement in 2D is often performed, where single diffraction patterns at the center of the Bragg peak ($\vec{q} = \vec{G}_{hkl}$) are collected for each probe position. These measurements take advantage of the fact that the measured intensity patterns of a 2D slice from a Bragg peak encodes wave field information about the projection of the sample along the exit direction $\vec{k}_f$, as described in literature [239]. This technique is known as 2D Bragg ptychography or Bragg projection ptychography. This measurement allows for the reconstruction of 2D projections of the strain field in the sample with a resolution better than the probe size. Two dimensional Bragg ptychography has been very useful for visualizing strain states in nanocrystals [240, 239, 241], but is insufficient for samples that require 3D strain analysis.

2.4.3.3. 3D Bragg projection ptychography. In recent years, a new approach to 3D Bragg ptychography has been developed that enables more efficient 3D strain measurements. This method, called 3D Bragg projection ptychography (3DBPP), formulated by Charmard, Allain, and Hruszkewycz, allows for the reconstruction of 3D displacement fields using a single diffraction angle at each probe position [242]. In 3DBPP, the phase field information along the projection direction is reconstructed by utilizing the translational variance in the X-ray probe (as opposed to rotational variance from rocking curves collected in 3D-BP). The schematic in Figure 2.9 depicts the relationship between real space and reciprocal space directions for a ptychography measurement. In this example, a thin film is illuminated at a Bragg condition by incident beam $\vec{k}_i$. The scattered exit beam $\vec{k}_f$ is collected on a 2D area detector recording the projection of the sample and probe along $\vec{k}_f$ (in purple). A detector reference frame is established where the $\vec{r}_z$ is parallel to $\vec{k}_f$ and $\vec{r}_x$ and $\vec{r}_y$ are in the detector plane. At the detector, $\vec{r}_x$ and $\vec{r}_y$ are equivalent to

the reciprocal space directions $\vec{q}_x$ and $\vec{q}_y$. The probe is then scanned normal to its propagation direction, which constitutes a shift in the reconstruction reference frame of a partial component in $\vec{r}_x$ and a partial component in $\vec{r}_z$. Therefore the third reciprocal space dimension $\vec{q}_z$ is probed through the scanning of the probe with a component along $\vec{r}_z$. Note that this $\vec{r}_z$ component becomes very small at small incident angles (θ).

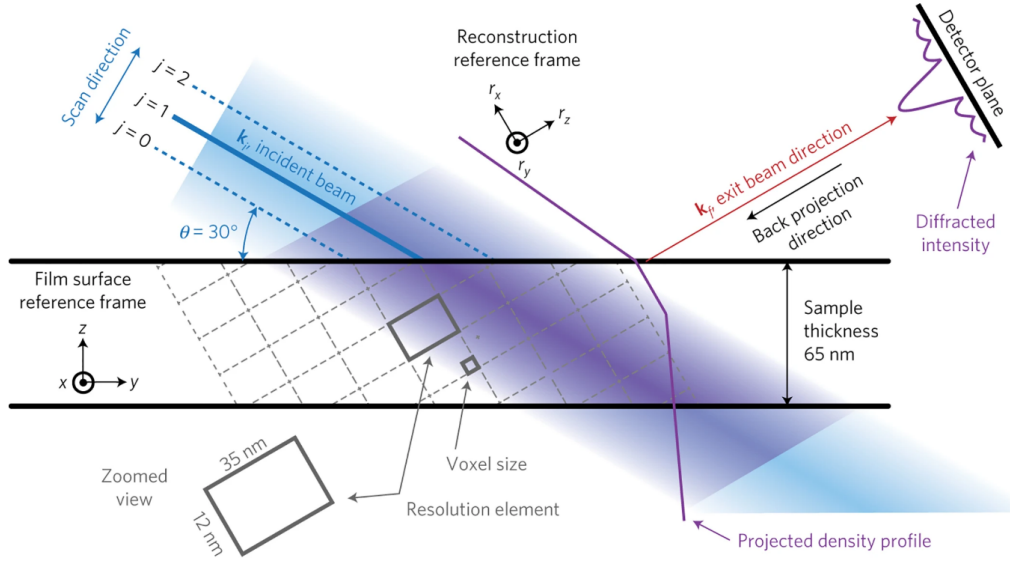


Figure 2.9. Schematic of 3DBPP scattering geometry. A reference detector frame is established where $\vec{k}_f$ (the exit direction and projection direction) is parallel to $\vec{r}_z$, and the detector plane is in $\vec{r}_x$ and $\vec{r}_y$. The 2D intensity patterns recorded at the center of the Bragg peak encode reciprocal space information about $\vec{q}_x$ and $\vec{q}_y$. The probe is stepped with a component along $\vec{r}_z$, probing the 3rd reciprocal space dimension $\vec{q}_z$. A new voxel grid for the reconstruction is defined with reference to the detector. The resolution element along $\vec{r}_z$ is related to the step size of the probe. Reprinted with permission from reference 242, Copyright © 2016, Springer Nature.

The formulation of 3DBPP can be easily extended from Eqn. 2.34:

$$(2.35) \quad \psi_r^{2D} = \mathcal{F}\mathcal{R}(P_r^{3D} \cdot \rho^{3D})$$

where $\mathcal{R}$ is the projection operator, which sums the projection across the projection direction $\vec{k}_f$ which is localized to the interaction volume of the probe and sample. Going from a 2D scattered amplitude back to the 3D object is described by:

$$(2.36) \quad P_r^{3D} \cdot \rho^{3D} = \mathcal{F}^{-1}\mathcal{R}^\dagger \psi_r^{2D}$$

where $\mathcal{F}^{-1}$ is the inverse FFT, and $\mathcal{R}^\dagger$ is the backprojection operator, which stretches the 2D projection back along $\vec{k}_f$. Figure 2.10 outlines the typical process of phase retrieval for 3DBPP. A random guess of amplitude $|E_1|$ and phase ϕ_1 defines the 3D crystal density ρ_1^{3D} . Next, the probe function P_{r_j} is applied (P_{r_j} is also 3D) then $P_{r_j}\rho_1^{3D}$ is projected along $\vec{k}_f$ using projection operator $\mathcal{R}$ to define a convolved real space density function in 2D: $\mathcal{O}_{r_j n}^{2D}$. A 2D-FFT converts $\mathcal{O}_{r_j n}^{2D}$ to reciprocal space defining the 2D scattering wave field at the j^{th} probe position r_j . The scattering amplitudes are replaced by the square root of the 2D diffraction pattern collected at that probe position r_j . An inverse FFT converts this back to real space, giving a new 2D real space amplitude and phase field $\mathcal{O}_{r_j n+1}^{2D}$. $\mathcal{O}_{r_j n+1}^{2D}$ is then back-projected (“stretched”) along $\vec{k}_f$ using the back-projection operator $\mathcal{R}^\dagger$ and a fixed real space support is used to constrain the extent of back-projection within the sample volume. This 3D density is used to locally update the phase and amplitude in ρ_n^{3D} . This process repeats for the next probe position $j+1$, until all the probe positions R have been used to locally update ρ_n^{3D} . This updated ρ_{n+1}^{3D} is then used to repeat this process for N iterations, until converging to the solution ρ_N^{3D} . This process is notably different than the phase retrieval process for 3D-BP, outlined in Figure 2.8 in two ways. First, the iterations between real and reciprocal space are performed in two dimensions. The use of 2D FFTs significantly reduces the computation cost of this phase retrieval process. Second, a fixed real space support must be applied after the back-projection before locally updating the density function ρ_n^{3D} . This is because the projection direction $\vec{k}_f$ is insufficiently constrained in reciprocal space without the use of angular rotation. Therefore, some *a priori* knowledge of the sample is required, at least along the projection direction. 3DBPP has been demonstrated on $\text{Si}_{0.8}\text{Ge}_{0.2}$ periodic films embedded between silicon-on-insulator (SOI) channels [242]. The (004) SiGe diffraction condition was used to reconstruct the 3D strain field associated with the SiGe/SOI interface with an estimated asymmetric spatial resolution of 12, 29, and 35 nm ($\vec{r}_x$, $\vec{r}_y$, and $\vec{r}_z$ respectively).

2.4.3.4. Limitations and challenges of Bragg projection ptychography. 3DBPP offers the ability to map the 3D strain of extended objects without the impractical data collection times of 3D-BP. Further, 3DBPP removes the strict constraint of precise probe alignment between angles, as required in 3D-BP. However, a major limitation of 3DBPP is that the phase retrieval process is not highly constrained.

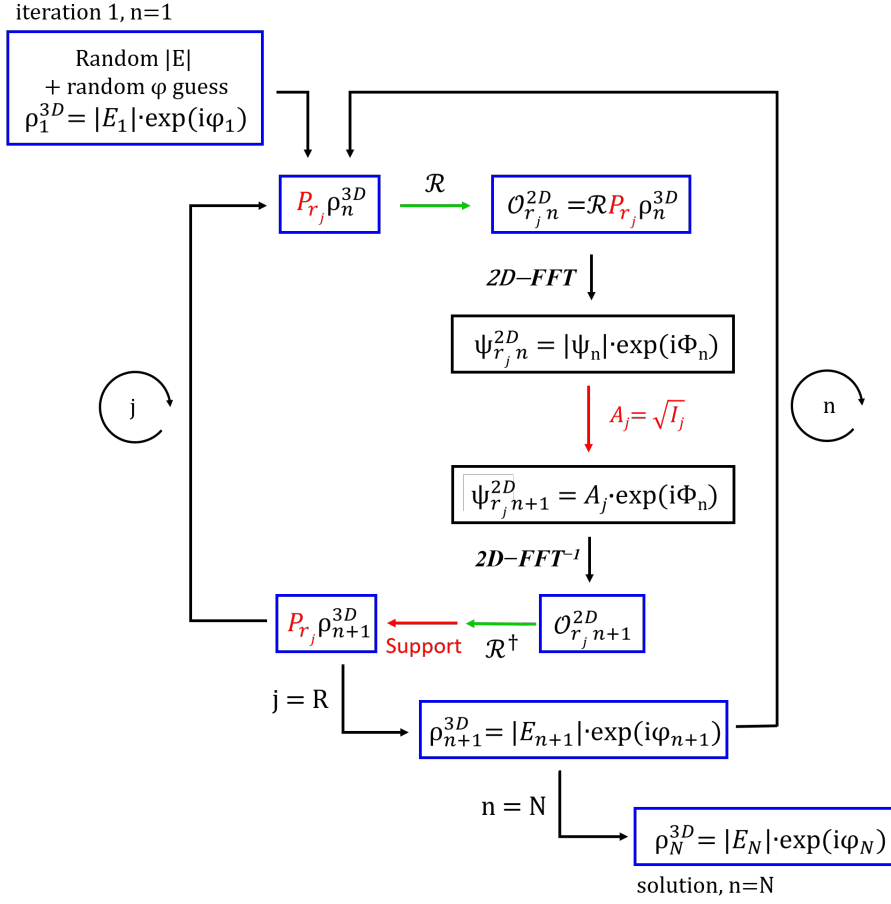


Figure 2.10. Typical process flow for phase retrieval in 3D Bragg projection ptychography. Real space and reciprocal space steps are shown as blue and black boxes respectively. Red arrows or highlights denote application of constraints. Green arrows denote application of projection or back-projection operator. 2D-FFT and 2D-FFT⁻¹ denote 2D fast (inverse) Fourier transforms.

In order to produce sufficient constraints for reconstruction of a 3D phase field, 3DBPP measurements must be performed at high incident angle $\vec{k}_i$, such that the scanning direction (normal to the incident probe) has a sufficiently large component along $\vec{r}_z$. In the experimental example of 3BPP mentioned previously, the first order ($n=1$, $n(\text{hkl})$) out-of-plane reflection for $\text{Si}_{0.8}\text{Ge}_{0.2}$ is (004), which scatters at a high incident angle (30.2° at 9 keV). However, for most crystal structures, the first order scattering ($n=1$) occurs at much lower incident angle. For instance, ZB GaAs (111) scatters at an incident angle of 12.2° at 9 keV, giving insufficient access to the $\vec{r}_z$ direction for 3DBPP reconstruction. Scattering

at the 2nd order peak (333) would allow for an incident angle of 39.2° , which is sufficiently high for 3DBPP reconstruction, but the (333) reflection scatters with only $\sim 8\%$ of the intensity of (111) [175]. So for a weakly scattering crystal, the higher order reflections are difficult to measure. Additionally, the high incident angles needed for 3DBPP not always accessible at a given beamline due to the geometric constraints. Therefore, a ptychography method is desired that retains the reasonable measurement times and flexible probe positions in 3DBPP, while introducing additional constraints on the phase retrieval process.

In Chapter 4, such a method is formalized and experimentally demonstrated. An extension of 3DBPP, multiangle Bragg projection ptychography (maBPP) uses the same general phase retrieval process outlined in Figure 2.10 but allows for the addition of scattering angles away from the Bragg peak center ($\vec{q} \neq \vec{G}_{hkl}$). For maBPP, the relationship between the 2D scattered wave function ψ_r^{2D} and the 3D real space density function ρ_j^{3D} can be described as:

$$(2.37) \quad \psi_r^{2D} = \mathcal{FR}(\mathcal{Q}_{\theta_j} \cdot P_{r_j} \cdot \rho^{3D})$$

where the term $\mathcal{Q}$ is defined in Eqn. 2.29. $\mathcal{Q}_{\theta_j}$ encodes the angular deviation from the Bragg peak at the θ angle of the j^{th} 2D diffraction pattern. The formulation of maBPP is described in more detail in Section 4.3. maBPP enables the use 2D intensity patterns collected at arbitrary probe positions (P_{r_j}) and arbitrary angles (θ_j). Unlike 3D-BP, maBPP does not require 3D diffraction patterns for each probe position, therefore the weakly scattering angles in the rocking curve do not need to be measured. Further, since each 2D diffraction pattern is used independently in the reconstruction, the probe positions at each θ angle do not need to align. Flexible probe alignment allows for the use of fast fly scanning [238] (which does not reproduce the exact probe positions at each angle) greatly reducing measurement time. In fact, slight misalignment in the probe positions between angles actually encodes additional real space overlap in the dataset.

In Chapter 4, maBPP is experimentally demonstrated for the first time. In this experiment, primarily-WZ InGaAs nanowires were imaged at two diffraction conditions. The first scattering condition, $(2\bar{1}\bar{1}0)$, allowed for reconstruction of the in-plane nanowire strain field in 3D. The other condition, $(01\bar{1}0)$, probed the phase change due to stacking variations in the WZ crystal. As discussed in Section 2.4.2.4, BCDI

has been shown to be insufficiently constrained to enable reconstruction in the presence of rapid phase variations created by stacking faults in nanowires. However, Chapter 4 shows that maBPP offers sufficient constraints to reproducibly reconstruct stacking fault phase variations within a limited region of a nanowire, with a maximum spatial resolution better than 2 nm. This work demonstrates that maBPP is a highly flexible extension of 3D Bragg ptychography capable of reconstructing complex strain fields at high spatial resolution. One challenge of maBPP, that inhibits its broad usage, is that it is difficult to formulate a generalizable experimental design for phase retrieval, as discussed in Section 4.4.

2.4.3.5. Conclusions: coherent X-ray imaging. In the last few sections, three approaches to 3D strain imaging using coherent X-rays have been discussed. Bragg coherent diffraction imaging allows for reconstruction of high spatial resolution (10-20 nm) strain field maps within single nanocrystals. It is however limited to nanocrystals that fit within the few micron coherent beam and cannot reconstruct rapidly varying phase features. Ptychography is proposed for mapping strain fields in extended crystals. 3D Bragg ptychography is theoretically very robust to complex phase problems, but typically 3D-BP datasets take impractical amounts of time to collect. 3D Bragg projection ptychography was introduced as a flexible alternative to 3D-BP. 3DBPP uses 2D diffraction patterns collected at the Bragg peak maximum and a real space support to back-project the “lost” third dimension in reciprocal space that is normal to the detector plane. However, 3DBPP is limited to high incident angles to sufficiently constrain the phase retrieval. Finally, multiangle Bragg projection ptychography was briefly introduced. This technique allows for arbitrary angles and probe positions to be combined in the phase retrieval process, increasing the number of input constraints compared to 3DBPP while maintaining experimental flexibility. While continued technique development is necessary, coherent X-ray imaging has proved to be a powerful technique for probing strain embedded in crystals non-destructively.

2.4.4. Nano-probe X-ray Diffraction

In the cases where 3D strain mapping is not possible or not required, X-ray nano-probes can still be very powerful tools for analyzing the strain state in nanocrystals. Scanning X-ray diffraction microscopy

(SXDM) using a nano-focused beam, sometimes referred to as nanoXRD, involves scanning a nano-focused X-ray beam (coherency not required) across a sample and recording a diffraction pattern in the Bragg condition for each probe position. The position of the Bragg peak in the detector is mapped as a function of probe position. The angular deviations in the Bragg peak represent deviations in the crystal lattice, including lattice strain and tilt.

In the example SXDM measurement by Calvo-Almazán, et. al. [243], tilt and strain in the (111) lattice planes were measured within individual CdTe grains. The detector was placed at a 2θ angle of 21.2° to collect diffraction signal from the (111) Bragg peak. The polycrystalline CdTe film consisted of grains at a wide range of orientations, so at the incident angle, only a single grain within the 100 nm probe fulfilled the Bragg condition. A coarse rocking curve (0.05° steps) was collected at each probe position. While SXDM does not require 3D diffraction patterns to map strain variations, it is important to identify the angle at which the detector slice is at the center of the Bragg peak ($\vec{q} = \vec{G}_{hkl}$). Since this condition may be met at slightly different angles throughout the sample (due to bending of the crystal planes), it is most practical to collect 2D diffraction patterns at a range of angles. Figure 2.11(a) shows a rocking curve that maps the integrated intensities at all scanning positions in a grain at each θ angle, with the highest intensity point being the Bragg angle. For a single scanning position the 2D diffraction pattern at the Bragg angle is shown in 2.11(b). The centroids of the diffraction patterns in the x and y positions of the detector are shown in 2.11(c). These centroid values must be converted to angular variations radially and azimuthally with respect to the Debye-Scherrer (DS) ring (marked in green). Analogous to powder diffraction, variations azimuthally along the DS ring are due to tilting of the crystal planes. Deviations of the Bragg peak radially from the DS ring are the result of changes in d-spacing, due to strain. The detector pixels can be converted to angles using Eqn. 2.31. For the CdTe grain in this example, the radial and azimuthal angle of the centroids are seen in 2.11(c). The azimuthal centroids angles are normalized to produce a relative lattice tilt as seen in the top of 2.11(d). The lattice spacing can be calculated from the radial centroid angles according to Bragg's Law:

$$(2.38) \quad d_{111} = \frac{\lambda}{2\sin(\theta_{radial}/2)}$$

as seen in the lower image of 2.11(d). The strain with respect to the known lattice spacing d_0 is then simply:

$$(2.39) \quad \epsilon_{111} = \frac{d_0 - d_{111}}{d_{111}}$$

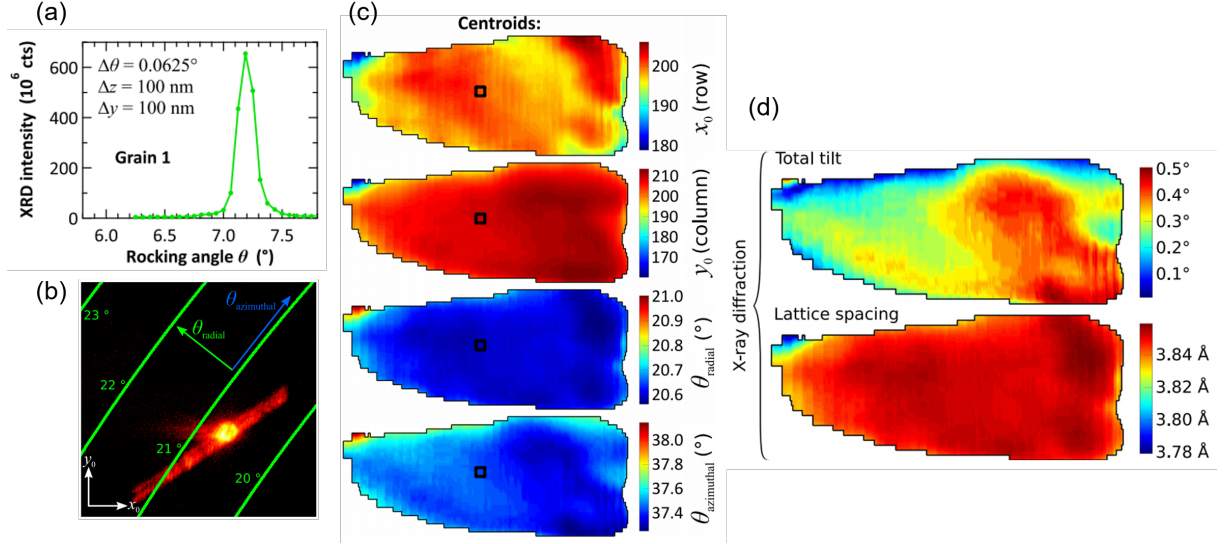


Figure 2.11. Example of scanning X-ray diffraction microscopy. (a) Rocking curve of integrated diffraction intensities. (b) Example 2D diffraction pattern at Bragg peak maximum. (c) x,y centroids of Bragg peak in the detector (top). Centroids are converted to radial and azimuthal angular deviations with respect to the known Debye-Scherrer ring. (d) Azimuthal centroids are normalized to relative crystal lattice tilt (top) and radial centroids are converted to lattice spacing (bottom). Reprinted with permission from reference 243 Copyright © 2019 IEEE.

As shown through the example of CdTe, SXDM can map strain variations with high spatial resolution (dependent on the probe size) with strain sensitivities better than 10^{-3} . A few examples of nanowire strain and lattice tilt mapping using SXDM can be found in literature [244, 245, 246]. The resolution of SXDM is dependent on the probe size, and therefore benefits from recent advances in X-ray focusing optics. Since SXDM produces 2D projections of lattice spacing, it is critical to compare measurements to modeling of 3D strain in nanoheterostructures. Further, direct comparison of diffraction patterns collected during an SXDM measurement to simulated kinematic scattering diffraction patterns allows for better interpretation of potential artifacts such as defocus of the nano-focused X-ray beam. SXDM

measurements are often collected in parallel with Bragg ptychography measurements and can be useful to interpreting the lattice displacement fields generated in ptychography reconstructions.

2.5. Simulating Strain and Diffraction in Nanowires Heterostructures

The next section will outline approaches to imaging strain and crystal structure in nanostructures. However, it is first important to understand what strain is expected in a given heterostructure, dependent on its composition, geometry, and crystal structure. This section will review a method of strain simulation in nanostructures using finite element modeling (FEM). Some discussion will be given to simulations of incoherent growth (defect formation). Last, kinematic scattering simulations used to convert strain profiles to predicted diffraction patterns will be described.

2.5.1. Misfit strain in thin films and nanowires

The stress at the heterointerface of a thin film and substrate has been studied extensively. The primary source of stress in InGaAs grown on GaAs is the misfit strain due to the difference in lattice constants (a), given by:

$$(2.40) \quad \epsilon_{misfit} = \frac{a_{film} - a_{substrate}}{a_{substrate}}$$

This equation holds when the growth is fully coherent (no defects). For a large substrate, it is expected that this stress will be fully accommodated by the thin film, and the residual stress in the film is given by:

$$(2.41) \quad \sigma_{film} = -\frac{E_{film}}{1 - \nu_{film}} \epsilon_{misfit}$$

where E is the Young's modulus and ν is the Poisson ratio of the film. This equation only holds if the substrate is much larger than the film. In this case of an anisotropic film, this expression becomes a tensor equation [247, 248].

Interfacial strain cannot be calculated as simply at the heterointerfaces of nanostructures for a number of reasons. First, the misfit film may be grown on multiple facets or a non-planar surface (hexagonal, in the case of III-As nanowires). Importantly, in the case of nanowire radial heterostructures, the core of the nanowire cannot necessarily be considered a fixed or infinite substrate. This is because the core may sometimes share the residual stresses caused by the misfit strain, which complicates understanding of strain in the heterostructure. Efforts have been made previously to predict strain in nanowires assuming a cylindrical nanowire shape [249, 250]. From these simulations, a few generalizations can be made.

First, it can be expected that for simulations of a nanowire with finite length, the strain far away from the nanowire end facets (a distance at least $2\times$ the core diameter [251]) is equivalent to the simulation of strain in an infinite wire, according to Saint-Venant's principle for composites [249, 252]. Secondly, if the nanowire core is much larger than the shell ($\sim 40\times$ thicker by the thin-film approximation [253]), then the core can remain fixed (as in the thin film case). However, it has been observed experimentally that strain on the core is unavoidable if the shell is two times thicker than the core [254, 255]. Between these two extremes of core $\gg$ shell and shell $>$ core it can be difficult to determine if the core will act as an infinite substrate; therefore it is best to assume the core can accommodate strain (is not fixed). For the nanowires investigated in this thesis, the core is never greater than 10 times the shell thickness, so an infinite core will not be assumed. Simulations of strain have been extended to hexagonal nanowire core-shell structures, but the complex geometry prevents the use of a closed-form analytical solution to determine the strain state. Thus, simulations described here numerically minimize the strain energy within a 2D/3D heterostructure via finite element methods [256].

2.5.2. Strain simulations using finite element modeling in COMSOL Multiphysics

For the example of a radial InGaAs quantum well embedded in a GaAs nanowire, the nanowire structure should be built to scale in 3D in an FEM software; in this case COMSOL Multiphysics was used. To minimize computational time, the nanowire length can be reduced, but should be made at least a four times longer than the nanowire diameter to fulfill Saint-Venant's principle. It has been found that Poisson effects dominate at the ends of the simulated nanowires, producing unrealistic bulging of the core out of the nanowire shell. As such, cuts from only the center of the nanowire should be taken for interpretation of the strain [251]. The simulation is unrealistic at the ends. The respective materials properties are applied to each segment in the geometry: in the example in Figure 2.12 the core and barrier are composed of GaAs and the interior shell/QW is $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$. The density and elastic constants for each material in the heterostructure can be determined using Vegard's law. Since elasticity is an anisotropic property, it must be properly defined with respect to the COMSOL geometry. For III-V nanowires, the elastic constants can be described by those of ZB cubic or WZ hexagonal crystals, according to the respective

tensors [257]:

$$C_{ZB} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ \cdot & C_{11} & C_{12} & 0 & 0 & 0 \\ \cdot & \cdot & C_{11} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & C_{44} & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & C_{44} & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & C_{44} \end{pmatrix} \quad C_{WZ} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ \cdot & C_{11} & C_{13} & 0 & 0 & 0 \\ \cdot & \cdot & C_{33} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & C_{44} & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & C_{44} & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & \frac{C_{11}-C_{12}}{2} \end{pmatrix}$$

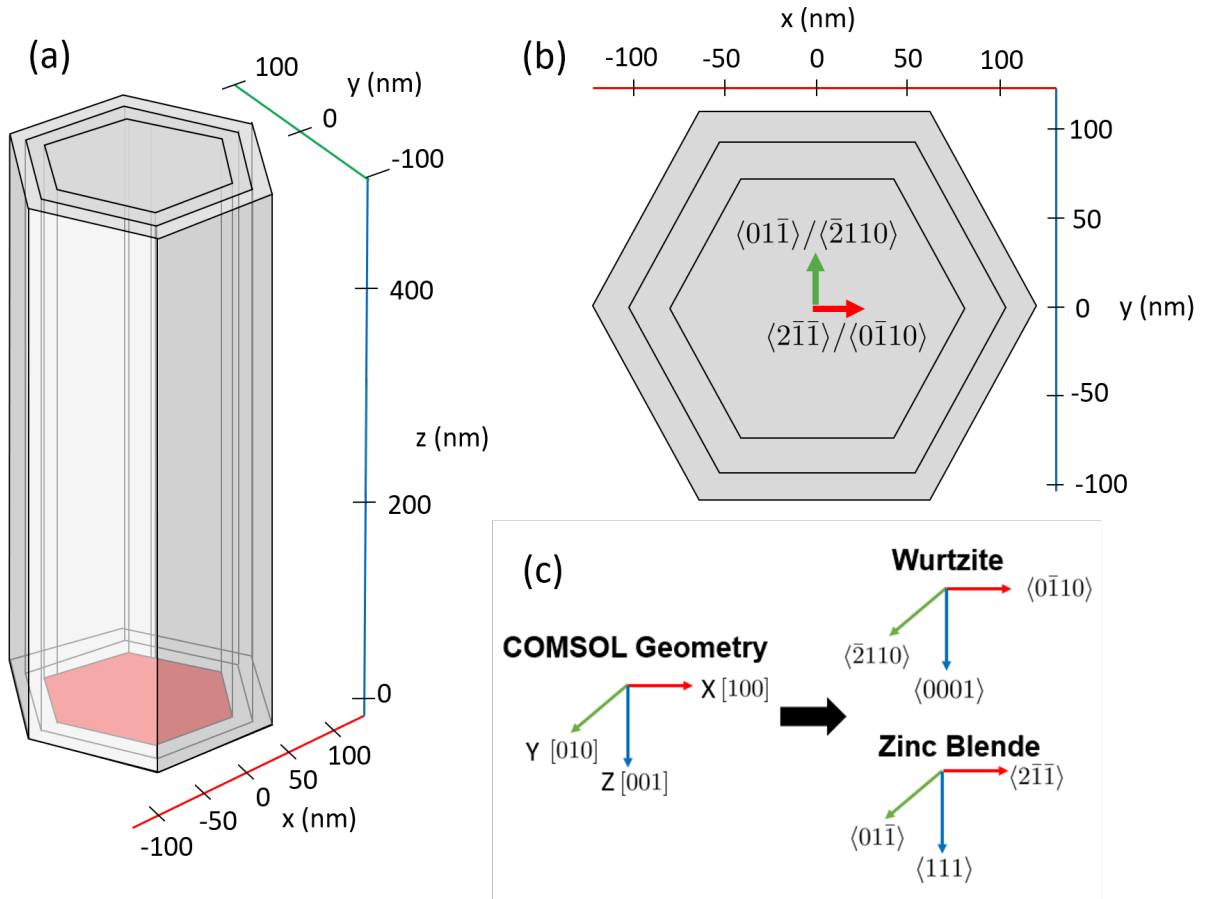


Figure 2.12. Model of strain in core-multishell nanowire by FEM in COMSOL. (a,b) Geometry of the 3D model. (a) Red facet of the nanowire corresponds to the boundary condition, fixing the bottom facet of the nanowire core. (b) X,Y projection of 3D structure. X axis correspond to the ZB/WZ $\langle 2\bar{1}\bar{1} \rangle / \langle 0\bar{1}10 \rangle$ directions and Y axis to the ZB/WZ $\langle 01\bar{1} \rangle / \langle \bar{2}110 \rangle$ directions (c). Directions for transformation from the COMSOL geometry to the WZ or ZB geometries.

The tensor must then be transformed to align the crystallographic axes with those of the nanowire model in COMSOL according to 2.12(c). Lattice constants and elastic constants for example simulations were taken from the literature [258, 259, 260, 261, 262].

To simulate the difference in lattice parameter between the core and shell material, a unrealistically large thermal expansion coefficient (α) is assigned to each material, such that a small change in temperature (ΔT) will produce a large expansion or contraction to simulate the lattice mismatch. In this case, the GaAs core and barrier should have a thermal expansion $\alpha_{GaAs} = 0$ because the GaAs is treated as the zero-strain state. The InGaAs QW on the other hand should be made to contract as expected due to the negative lattice mismatch, thus the thermal expansion coefficient is set as:

$$(2.42) \quad \alpha_{s1} = \frac{a_{GaAs} - a_{InGaAs}}{a_{InGaAs}} \Delta T$$

in units of $[\frac{1}{K}]$, where a is lattice parameter and ΔT is an arbitrary temperature change. For any given number of shells, the expansion coefficient of each layer should be set relative to the core (GaAs in this case). Since lattice parameter is anisotropic for WZ crystals, the thermal expansion coefficient should also be treated as such.

Proper constraints must be applied to the FEM model, because the nanowire core cannot be fixed. The most realistic constraint, fixing the bottom face of the nanowire core, is applied to mimic the nanowire growth geometry where the nanowire core is fixed to a Si substrate. The rest of the core and the shells are kept unbound. In 2.12(a) the bottom facet of the nanowire core is highlighted in red. This region is set as a fixed constraint in the FEM model, meaning there can be no displacement within the red hexagon ($u=v=w=0$). The final boundary condition is that the displacement across the interfaces must be continuous. Next, a stationary (steady state), solid mechanics, linear elastic material physics model is utilized and a finite mesh is applied to the nanowire geometry [263]. Finally the strain $\epsilon_{thermal}$ is applied via an artificial thermal expansion upon raising the temperature ΔT . The potential elastic energy is given by

$$(2.43) \quad U = \int w dV = \frac{1}{2} \int \mathbf{e} \cdot \mathbf{C} \cdot \mathbf{e} dV$$

where $\mathbf{e}$ is the elastic vector and $\mathbf{C}$ is the elastic constant tensor. Minimizing this potential energy universally by modifying the displacement of each free mesh component within the FEM model will

produce the predicted displacement field of the 3D structure. Further details on this method can be found in literature [249, 255, 251, 262, 264]. The solution of this FEM model gives the lattice displacement field and resulting strain within the nanostructure. The displacement field along a singular direction is utilized for simulations of diffraction in Section 2.5.4. For this example from an $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$ QW embedded in GaAs, the results are shown in Figure 2.13(a,b), with cross-sections of the strain $\epsilon_{yy} / \epsilon_{01\bar{1}}$ (a) and the lattice displacement $u_{yy} / u_{01\bar{1}}$ (b).

The results of atom probe tomography analysis of composition can be used to build the FEM model. The varying composition across the 3D APT dataset is converted to a variation in lattice parameter (by Vegard's Law), and then to a variation in thermal expansion coefficient with respect to the lattice parameter of the core material (GaAs). Figure 2.13 shows an example APT cross-section of a GaAs/InGaAs/GaAs QW structure in terms of the inputted thermal expansion coefficient (2.13(c)), as well as the resulting strain field (2.13(d)) and lattice displacement (2.13(e)) generated from the FEM model. Since the surface of the APT volume is often not equivalent to the surface of the heterostructure, some modifications must be made for the modeling of compositional strain. The APT data can be incorporated into a more structurally accurate geometry by assuming a symmetric heterostructure. Models of compositional strain can either be directly compared to strain images generated by CDI/ptychography or diffraction can be simulated, assuming kinematic scattering, as described in Section 2.5.4. These simulated strain fields have been used in band structure modeling to help predict the electronic or optical properties of a given heterostructure [265, 266]. However, while FEM acts as a useful tool for predicting the strain state expected for a particular geometry and composition, it cannot be assumed to fully represent the true strain field in the structure. For instance, cross-sectional strain images in QW core-shell nanowires via GPA have shown deviations from FEM simulated strain fields possibly due to atomic roughing at QW interfaces that can lead to strain relaxation [108]. Further, for FEM simulation of WZ III-As nanowires, the elastic properties are primarily taken from first principles calculations, since WZ III-As is not available in the bulk form [267]. As such, simulations of band structure may be inaccurate if only incorporating the FEM simulated strain. The complexity inherent in these core-shell nanowires, as

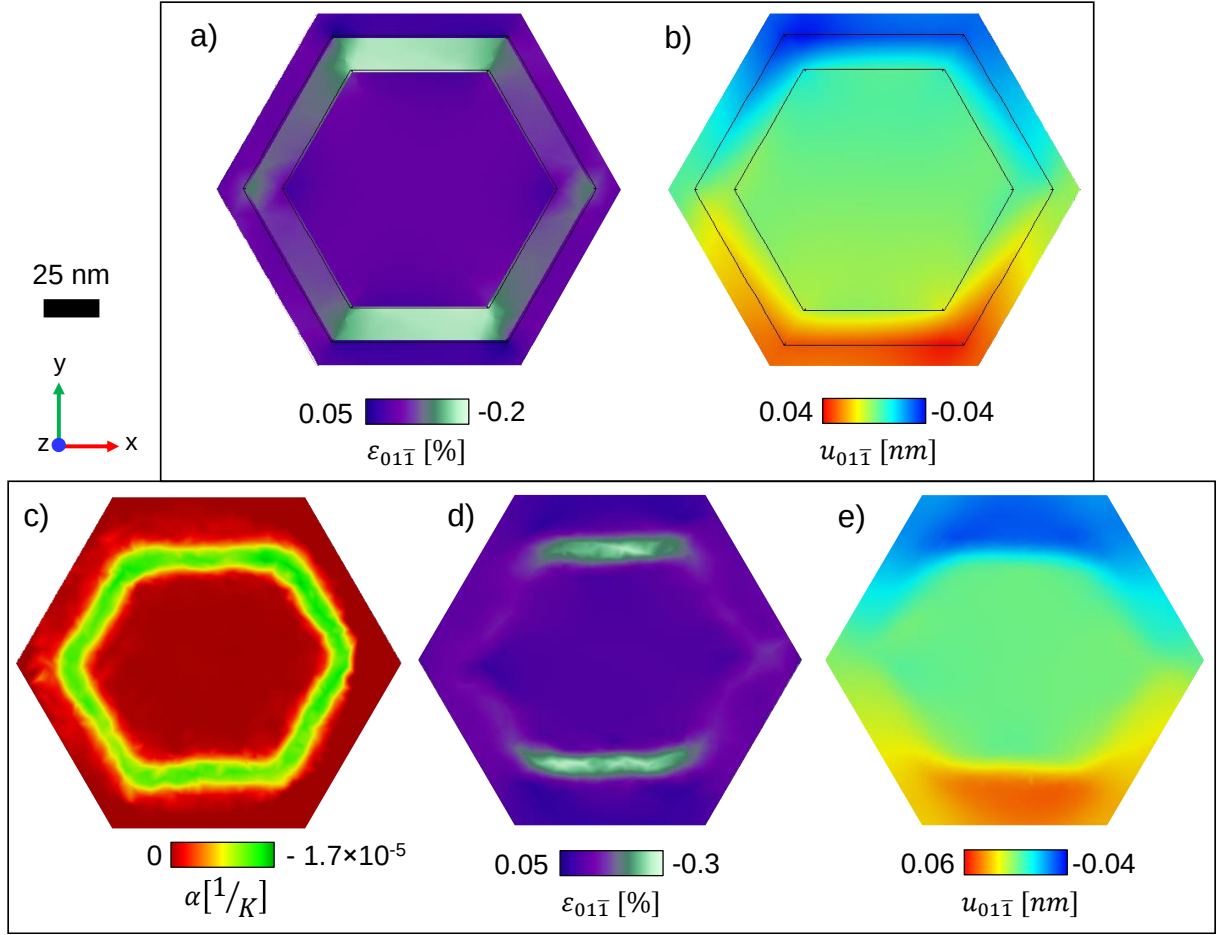


Figure 2.13. Example FEM simulations of nanowire QWs using nominal strain and APT as input. (a) 2D cut of strain ($\epsilon_{01\bar{i}}$) in InGaAs ($x_{In} = 0.25$) radial QW embedded in a GaAs nanowire by 3D FEM simulations. (b) Same cross-section converted to lattice displacement ($u_{01\bar{i}}$). (c) Cross section of 3D simulation of InGaAs QW in GaAs, displaying a fictitious thermal expansion coefficient determined by inputting APT data into FEM model. Same cross-section shown after raising the temperature of the simulation by ΔT , in terms of strain ($\epsilon_{01\bar{i}}$) (d) and lattice displacement ($u_{01\bar{i}}$) (e).

well as the many assumptions that must be made FEM simulations, highlights the need for direct strain imaging in single nanostructures.

2.5.3. Incoherent growth of core-shell heterostructures

Thus far, only the case of fully coherent growth has been considered. In these cases, the FEM model described above can be used, but the case of large misfit that cannot be fully accommodated by strain in the film or shell must also be considered. Stresses caused by misfit can be relieved in a number of ways, including dislocation formation, formation of antiphase domain boundaries, or film delamination/buckling [14, 268]. These strain accommodation mechanisms result in incoherent interfaces, thereby invalidating the FEM model presented above. Strain energy calculations are used to predict the dimensions and misfit strains at which defect formation is more energetically favorable than misfit accommodation through strain. For the case of a thin film, a closed form equation for such critical thicknesses was developed by Matthews et al. [269] and was used to predict critical layer thicknesses of InGaAs/GaAs films by Anan et al [270, 271]. This is outlined in Figure 2.14(a), where the critical thickness as a function of In content is plotted for an InGaAs QWs grown on bulk GaAs, in either the [111] or [001] directions (solid and dashed lines respectively) [271]. At In content and thickness combinations to the right of these lines, dislocations are expected to form.

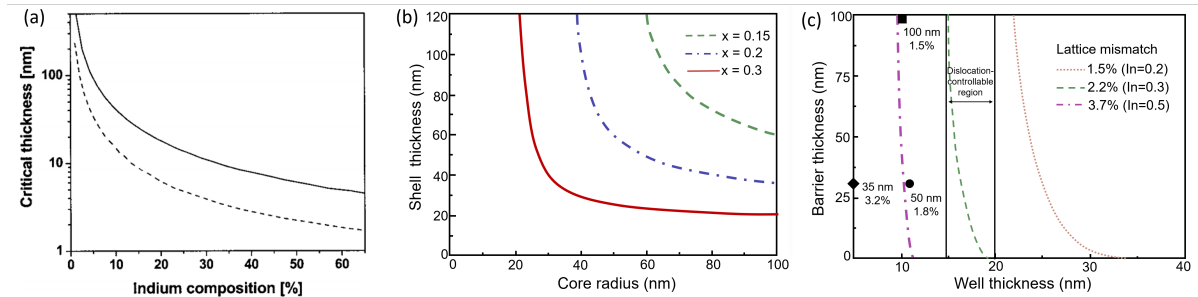


Figure 2.14. Comparison of critical thicknesses for InGaAs/GaAs films vs. core-shell nanowires. (a) The critical thickness of an InGaAs thin film as a function of In content for [111] (solid line) and [001] (dashed line) growth directions. (b) Critical thickness for dislocation formation in an InGaAs/GaAs core/shell nanowire. Dependence on both core radius and shell radius are shown. (c) Critical thicknesses for InGaAs QW embedded in GaAs with a core of 200 nm diameter. Dependence on both the QW thickness and the barrier thickness are shown. Experimental points are overlaid in black. (a) Adapted with permission from reference 271 © 2001 American Institute of Physics. (b/c) Adapted with permission from reference 107 © 2015, Springer Nature.

However, just as in the case of coherent growth, the understanding of defect formation in core-shell nanowires is more complex than in the thin film case. Numerous calculations and experimental studies have been performed to establish the conditions under which dislocations will form in core-shell nanowires, but there is no general predictive model. Examples of these energy calculations can be found in the literature [272, 273, 262]. For the case of InGaAs grown on GaAs, Yan et al. predicted that the formation of defects depends both on the core and shell of the nanowire (Figure 2.14(b)) since, as discussed in the previous section, if the nanowire core is thin enough it can also accommodate strain. The prediction of defect formation becomes even more complicated when considering an embedded InGaAs QW. In this case, as shown in 2.14(c), for a constant core thickness, the critical dimensions depend on the well thickness and the barrier thickness. Yan et al. also predicted an additional dependence on the core diameter for a embedded QW heterostructure (not shown here) [107]. However, the calculations were limited to a cylindrical geometry. Beyond the critical dimensions of defect formation, calculations have also been done to predict which type of dislocation (i.e. screw, edge loop, etc.) will form in III-As nanowire heterostructures, but no generalizable result has been presented [274, 275, 276], thus emphasizing the need for direct measurements of strain and structure in III-As nanowire heterostructures.

2.5.4. Kinematic scattering simulations

FEM simulations of strain can be directly compared with reconstructed strain fields in coherent diffraction imaging. In most cases, the strain field is convolved with a nano-focused X-ray beam or is reconstructed at lower resolution than in the FEM model due to limited diffraction signal or limited spatial resolution of the CCD X-ray detector. As such, it can be useful to simulate the expected diffraction from a given FEM model of strain using kinematic scattering simulations. These simulations are described below and more details can be found in literature [217, 277].

In X-ray diffraction, an incident X-ray beam ($\hat{k}_i$) is scattered from crystalline planes in a material, and the scattered waves along a single exit direction ($\hat{k}_f$) interfere constructively to produce a high intensity X-ray beam according to Bragg's law:

$$(2.44) \quad 2d\sin(\theta) = n\lambda$$

where d is the atomic plane spacing, 2θ is angle between the incident and exit beams, and λ is the incident X-ray wavelength. Bragg's law can also be formulated in terms of a momentum transfer $\hat{q}$ where:

$$(2.45) \quad \hat{q} = \hat{k}_i - \hat{k}_f$$

This momentum transfer is related to the lattice spacing by

$$(2.46) \quad |q| = \frac{2\pi}{d}$$

For a given diffraction condition, the displacement field (u) resolved in an X-ray experiment is the projection of the total displacement field along $\hat{q}$. Therefore, the displacement field of the FEM model along that direction is extracted for scattering simulations. As an example, consider an InGaAs QW / GaAs nanowire heterostructure, similar to that in Figure 2.13(a,b), though in this case with an In content of 15% and core diameter of 60 nm. The displacement along the $[01\bar{1}]$ direction ($u_{01\bar{1}}$) is extracted from the COMSOL model in order to simulate diffraction from the $(01\bar{1})$ crystal planes. The displacement field is then normalized by the d-spacing of the $(01\bar{1})$ planes to convert it to a phase field:

$$(2.47) \quad \rho = \frac{2\pi u_{01\bar{1}}}{d_{01\bar{1}}}$$

This phase field is then extrapolated across the length of a simulated nanowire (using MATLAB in this work) that is oriented in the appropriate scattering geometry to fulfill the $(01\bar{1})$ diffraction condition, as seen in Figure 2.15. The incident and exit beam are shown for the $(01\bar{1})$ scattering geometry. The phase field is extrapolated between the ends of the simulated nanowire onto a 3D grid of size: $N_{\text{pix}} \times N_{\text{pix}} \times \text{depth}$. For these scattering simulations N_{pix} refers to the number of pixels on the simulated 2D CCD detector.

In the case of scattering from an X-ray plane-wave (such as in coherent diffraction imaging), the complex 3D reciprocal space pattern for the nanowire is given by:

$$(2.48) \quad \psi_{3D} = \mathcal{F}^{3D} \rho$$

where $\mathcal{F}^{3D}$ denotes a 3D Fourier transform. Experimentally, CCD detectors only record intensity, not phase, so the diffraction intensity is simply $|\psi|^2$. This equation for conversion from real to reciprocal space holds in the case that only elastic scattering (no multiple scattering) occurs and the CCD detector is located in the far field (Fraunhofer diffraction) [278]. A single 2D diffraction pattern at the Bragg angle (as measured on the 2D CCD detector during an X-ray experiment) can be calculated as:

$$(2.49) \quad \psi_{2D} = \mathcal{F}^{2D} \sum_x \sum_y \rho$$

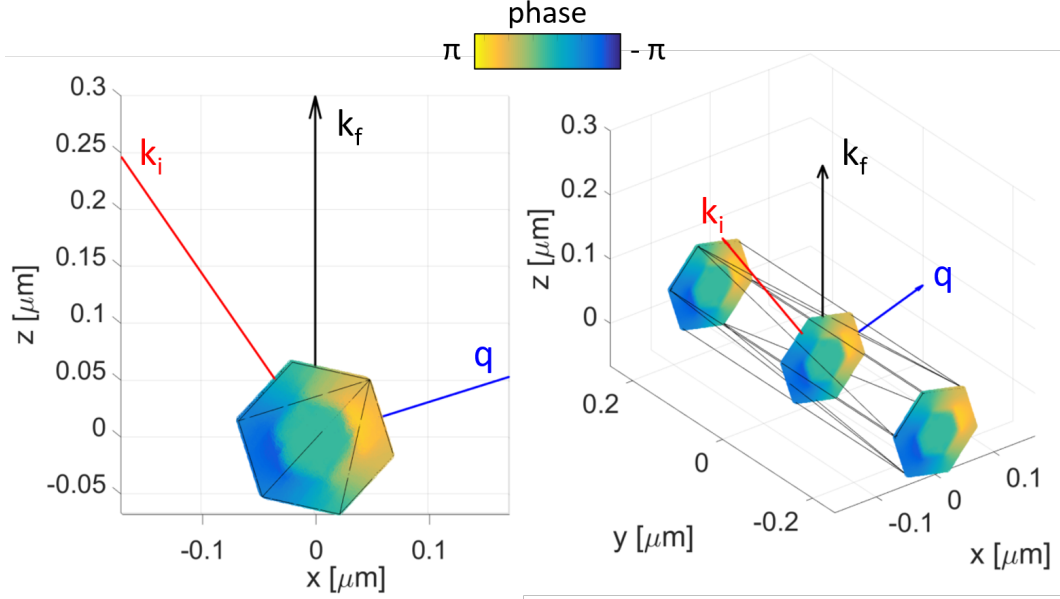


Figure 2.15. Example scattering geometry for kinematic scattering simulations. The COMSOL input is converted to phase and rotated to fit within a simulated nanowire structure. The phase input is extrapolated between the ends of the nanowire onto a 3D grid. Scatter vectors are shown with respect to the nanowire. This geometry corresponds to diffraction from the $(01\bar{1})$ planes.

Here $\mathcal{F}^{2D}$ denotes a 2D Fourier transform. The sum of the phase field ρ is taken over the X and Y directions because, for ease of calculation, the nanowire geometry was set that k_f is along the Z direction. As such, $\sum^x \sum^y \rho$ gives the projection of ρ as seen by the 2D detector.

In the case of nano-probe X-ray diffraction, simulations of the X-ray probe are required. In this case, a 2D image of an experimental probe (collected via transmission ptychography during an experiment [279]) can be extrapolated along k_i onto the same $N_{\text{pix}} \times N_{\text{pix}} \times \text{depth}$ grid as the nanowire. The cases in which an experimental probe is not available, simulations of the phase field of a diffraction limited beam can be utilized (simulated based on the type of focusing optic) [280]. The 3D simulation of the nano-probe can be shifted in the simulation window such that diffraction patterns from different positions (r) on the nanowire can be calculated. The probe is therefore position dependent (P_r). Diffraction from the simulated probe is given by:

$$(2.50) \quad \psi_{2D} = \mathcal{F}^{2D} \sum^x \sum^y P_r \cdot \rho$$

This will produce a 2D diffraction pattern which is the convolution of the probe centered at position r and the nanowire.

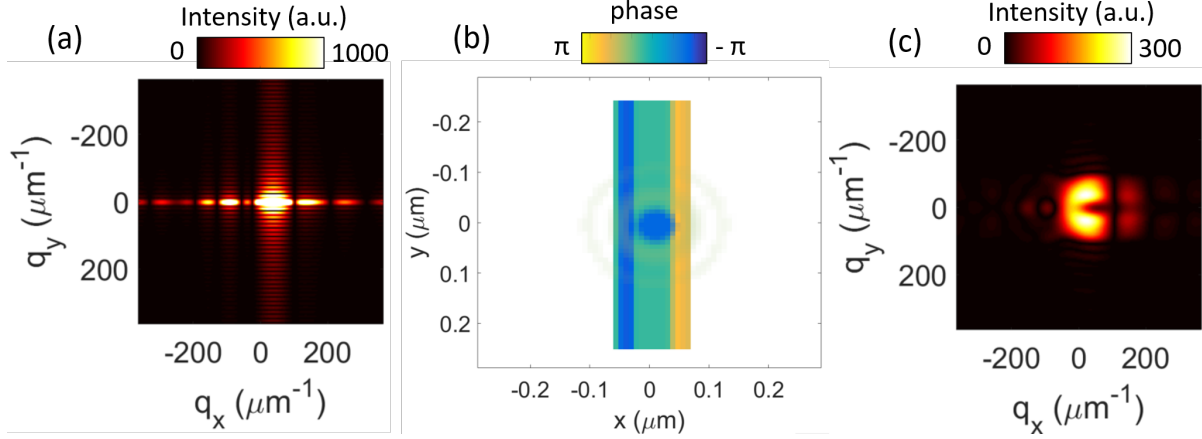


Figure 2.16. Example simulated diffraction patterns using kinematic scattering. (a) Diffraction at the $(01\bar{1})$ scattering condition using a X-ray plane-wave. (b) Real space projection of probe and nanowire phase field for the diffraction simulation in (c). (c) Diffraction at the $(01\bar{1})$ scattering condition using a nano-probe X-ray beam.

Examples of 2D plane-wave and 2D nano-probe diffraction for the nanowire and scattering geometry in Figure 2.15 are seen in Figure 2.16. In 2.16(a) the 2D diffraction pattern for the plane-wave simulation is shown. The high-frequency vertical fringes are a result of the crystal truncation rod produced by the top facets of the nanowire. The lower-frequency fringes are due to truncation from the nanowire side facets (defined by the nanowire diameter). In 2.16(b) the real space projection of the X-ray nano-probe in the detector plane is shown overlaid with the nanowire phase field. The simulation of nano-probe diffraction seen in 2.16(c) is from this probe position. As the nano-probe does not encompass the entire nanowire, no fringe patterns are observed. Instead, the diffraction is primarily defined by the doughnut shape of the X-ray nano-probe. It is notable that even given the same incident beam intensity, the diffraction from the nano-probe is much weaker than the plane-wave diffraction. In experiments, the nano-probe diffraction will be even weaker because the focusing optics are highly inefficient, limiting the incident flux of the X-ray nano-probe [281]. Noise can be added to the simulations to better compare with diffraction

patterns through addition of random shot-noise that is expected from the collection of photons on the CCD detector [282, 283].

2.5.5. Summary: strain and diffraction simulations in nanowires

Finite element modeling is a powerful method for simulating the strain at coherent interfaces in nanostructures of arbitrary geometries. These strain simulations can be incorporated into kinematic scattering simulations of diffraction with relative ease. Access to diffraction simulations of the sample of interest is critical for both planning and interpreting X-ray diffraction measurements. Simulating displacement fields becomes more complicated once defects or incoherent boundaries are introduced. FEM can nevertheless be a useful tool for recognizing when a nanostructure deviates from the expected coherent strain field, and thus when the presence of defects should be considered.

2.6. Electrical and Optical Characterization of Nanowires

In the next few chapters, composition, strain, and crystal structure in nanowires will be correlated with a number of different electrical and optical characterization methods. These correlations are necessary to understand the structure-property relationships and ultimately optimize the nanowires to produce the desired device characteristics. The property measurements used will be described briefly in this section.

In Chapter 3, the electrical behavior of single InAs nanowires is investigated. Seebeck coefficient measurements are performed to extract carrier concentrations from nanowires of different nominal Si-dopant concentrations. These measurements involve contacting a single nanowire on either end with Ni contact pads and fabricating a Ni resistive heater in close proximity to one end of the nanowire. By heating the resistor, a temperature gradient is applied across the nanowire length. The temperature and the Seebeck voltage is measured on each end of the nanowire using the Ni contacts. The slope of the Seebeck voltage as a function of temperature change gives a Seebeck coefficient (S) which can determine the carrier type (p-type if positive, n-type if negative). Additionally, the carrier concentrations can be estimated by comparing the Seebeck coefficient to the numerically calculated dependence of the Seebeck coefficient on carrier concentration using the Boltzmann transport equation [284]. In addition to Seebeck coefficient measurements, nanowire field effect transistor (NW-FET) measurements can be used to estimate carrier concentration. A NW-FET consists of a nanowire drop-casted onto a substrate which acts as a gate (such as $\text{SiO}_2/\text{n}^+\text{-Si}$) and contacted by four Ni/Au Ohmic contacts. Temperature dependent four-terminal transport measurements are then conducted, and the threshold voltage can be used to directly extract the carrier concentration [285]. These types of electrical measurements, among others, are important for understanding the activation of dopants in nanowire structures.

Since the nanowires investigated in this thesis are primarily intended as compact emitters, the main property measurements used are photoluminescence (PL) or cathodoluminescence (CL). Luminescence refers to the emission of photons from a material due to the excitation and subsequent decay of electrons. In PL the source of excitation is electromagnetic radiation (photons) and in CL the excitation comes from an electron source (such as a SEM or TEM beam).

Generally, PL spectroscopy refers to the measurement of the emitted photon energy distribution after optical stimulation. When the energy of incident photons is larger than the bandgap of a semiconductor, electrons are excited into the conduction band. Relaxation will occur through both radiative (photons) and non-radiative (heat:phonons) recombination processes. For PL of a homogeneous, defect-free, direct bandgap semiconductor, a narrow emission peak centered around the bandgap energy is expected, as the emission is due to the radiative recombination of electron-hole pairs across the bandgap. Changes in strain or composition will modify the position and width of the emission. Additionally, defects or impurities can act as sites for non-radiative recombination events reducing the overall luminescence. As such, PL is a useful tool for both understanding emission and probing structure and defect sites in materials. Extensions of conventional PL such as time-resolved, temperature dependent, or power dependent PL measurements allow for the evaluation of different excitation states and time dependent phenomena such as carrier transport within a heterostructure. Additionally, taking spectral series (with variable power, temperature, or excitation wavelength) allows for the deconvolution of the many features that contribute to a single PL spectra. Further details of the measurement and interpretation of semiconductor photoluminescence is found in the literature [286, 287, 288].

Cathodoluminescence can also be used to spatially resolve optical properties of semiconductors. The primary difference with PL is the use of higher energy excitation (via electrons) and a much smaller probe for stimulation (typically < 5 nm as compared to > 500 nm in PL). CL performed in an SEM or TEM allows for excitation at a single point (though emission throughout the sample is collected simultaneously). Maps of emission energy or intensity due to localized excitation can be created using spatially resolved CL [289, 290, 291]. This is useful for investigating complex films or nanostructures because it deconvolves emission that results from excitation in different regions of the sample. The same careful analysis of emission spectra required in PL is also necessary for CL measurements [292].

The ultimate goal of the nanowire research pursued in this work is to enable these materials to lase in the infrared. Eventually, electrical pumping of nanowires is desired to produce optical emission, but in the near-term, optical pumping (such as used in PL) is a useful tool for probing stimulated emission (lasing) in nanowires heterostructures. Many examples of optically pumped nanowire lasers have been

demonstrated, including for bare GaAs [51, 293], GaAs/AlGaAs heterostructures [294, 99], and, with limited success, In(Al)GaAs/GaAs heterostructures [295]. The PL and CL measurements described here are necessary to understand the optical quality of a particular nanowire heterostructures and gauge the progress towards creating efficient compact emitters.

CHAPTER 3

Composition and Dopant Mapping in InAs Nanowires

3.1. Motivation of Research

Control of doping of III-As nanowires is necessary for the formation of low resistance contacts for electronic and optoelectronic devices. Dopants are typically incorporated during the nanowire growth process (*in-situ*). Because nanowire growth relies on inherent anisotropies in incorporation between different facets, inhomogeneous dopant profiles are not uncommon [296], as discussed in Section 1.4.2. For instance, inhomogeneous doping of P in Ge nanowires has been observed due to preferential incorporation on truncation facets at the solid-liquid interface [69, 297]. A qualitatively similar segregation was reported for Si in GaAs nanowires, but attributed to competing incorporation by VS growth on the nanowire sidewall [32]. Ultimately, achieving uniform doping requires a detailed understanding of the growth process. Doping of III-V nanowires is particularly challenging due to the amphoteric nature of group-IV dopants like Si and Ge in III-Vs [298] which can lead to carrier compensation [299]. For example, changes in III-V precursor ratios and growth temperatures to control the growth rate and morphology may influence the dopant type as a side effect. Therefore, we not only need to understand the spatial distribution of dopants in III-As nanowires, but the extent of carrier activation, determined through electrical or optical measurements. A correlative atom probe and electrical measurement study of Si dopants in InAs is presented below, modified with permission from J. Becker, **M.O. Hill**, et al. “Correlated Chemical and Electrically Active Dopant Analysis in Catalyst-Free Si-Doped InAs Nanowires” ACS Nano 12.2, (2018): 1603-1610. Copyright © 2018 American Chemical Society.

3.2. Introduction

The realization of high-performance electronic and optoelectronic devices from semiconductor nanowires makes accurate control of charge carrier conductivity by intentional doping indispensable. Understanding

doping behavior and establishing links between dopant distribution and carrier activation in free-standing nanowires is, however, still a challenging task. The three-dimensional, high aspect-ratio structure of nanowires possesses axial and radial growth facets with different crystal orientations, surface reconstructions, and hence highly anisotropic growth dynamics, which are expected to influence dopant incorporation. [297, 68, 300] In many cases, these characteristics are complicated by fundamentally different growth modes of the participating facets. For example, in the predominantly studied catalyst-assisted vapor-liquid-solid (VLS) growth of nanowires, dopant incorporation can proceed either via the liquid catalyst interface [301, 302], the solid sidewall facets [73], or by a combination of both facets, as recently demonstrated e.g. for VLS-grown Si nanowires [297, 303] and GaAs nanowires [32]. In VLS-grown nanowires it has been also shown that dopant incorporation and carrier activation are directly affected by the peculiar crystal phase polytypism commonly observed in III-V semiconductor nanowires. Both experimental and theoretical studies revealed that Si-doping of wurtzite (WZ) phase GaAs nanowires results in p-type conductivity as opposed to n-type conductivity in Si-doped bulk zincblende (ZB) GaAs [304, 305]. Doping of VLS-type III-V nanowires has also profound effects on the crystal phase stability and defect structure itself. For example, doping of III-V nanowires can alter the crystal phase from WZ to ZB [306] and vice versa [307], allowing the formation of complex twin-defect nanowire superlattice structures [306]. In addition, the presence of specific planar defects in the nanowire may also trap dopant impurities via the catalyst interface [308], modifying their electrical activity. Compared to VLS-grown nanowires, much less attention has been paid to dopant incorporation studies of catalyst-free, *i.e.*, non-VLS type nanowires. This is because the non-catalytic spontaneous growth mode is limited mostly to nanowires from the group-III nitride [300, 309, 310] and III-V arsenide families grown under selective area epitaxial processes [34, 311, 33, 35]. Whilst most doping studies of these classes of nanowires focused on the effects of dopants on morphology, microstructure, and basic transport properties [311, 312, 313, 314, 315], correlated studies between dopant concentration and distribution, and carrier activation has remained quite limited [300] due to challenges in probing dopants with atomic resolution in nanowires. In this work, we demonstrate a direct correlation between chemical and active dopant concentrations in n-type Si-doped InAs nanowires grown by molecular beam epitaxy (MBE) in a completely catalyst-free, *i.e.*, vapor-solid (VS) type growth

mode. Essentially, we employ local electrode atom probe tomography (APT) to map the Si dopant density and distribution in single nanowires, and compare data with active carrier concentrations probed by Seebeck effect and four-terminal nanowire field effect transistor (NW-FET) measurements.

3.3. Results and Discussion

3.3.1. Growth and structural characterization of nanowires

The growth of the InAs nanowire samples was carried out in a solid source Gen-II MBE system equipped with standard effusion cells for group-III elements (Al, Ga, In) and a valve cracker cell supplying molecular arsenic (As_4). 2-inch [111]-oriented Si wafers were used as growth substrates, which were covered with a $\sim 2\text{-}5$ nm-thick and wet chemically etched SiO_2 layer. The etched SiO_2 layer provides a mask for nucleating nanowires in a selective-area like manner from random nm-sized pinholes [316]. Typical examples of the non-catalytic vertical growth of InAs nanowires on this growth substrate are shown by the scanning electron micrographs (SEM) in Fig.3.1, for cases of (a) undoped nanowires and (b) highly Si-doped nanowires for comparison. No metallic In droplets are present on the nanowire tips, confirming the catalyst-free vapor-solid (VS) growth mode of these nanowires [316]. The depicted nanowire samples are part of growth series performed under identical growth conditions but variable Si-dopant fluxes (see Supporting Information for respective SEM images). Specifically, we used an In-flux of $0.36 \text{ \AA/s}$ and an As_4 -flux of $14 \text{ \AA/s}$ (beam equivalent pressure of $2.6 \times 10^{-5} \text{ mbar}$), corresponding to a V/III ratio of ~ 40 [102]. Growths lasted for 90 min at a growth temperature of 500°C . Atomic Si dopants were supplied continuously during growth, except for the very first 5 min to prevent any Si-induced effects on the nucleation. The Si dopants were provided by a solid dopant cell via thermal sublimation induced by resistive heating of the cell. Besides an undoped InAs nanowire reference, three Si-doped nanowire samples were grown with different cell heating currents (11A, 12A, 13A), where the highest current corresponds to a Si dopant flux of $\sim 1.6 \cdot 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ [32]. Note that a linear increase in heating current means an exponentially increasing Si dopant flux, as confirmed by secondary ion mass spectrometry (SIMS) on planar reference samples. Specifically, the three respective heating currents correspond to Si dopant

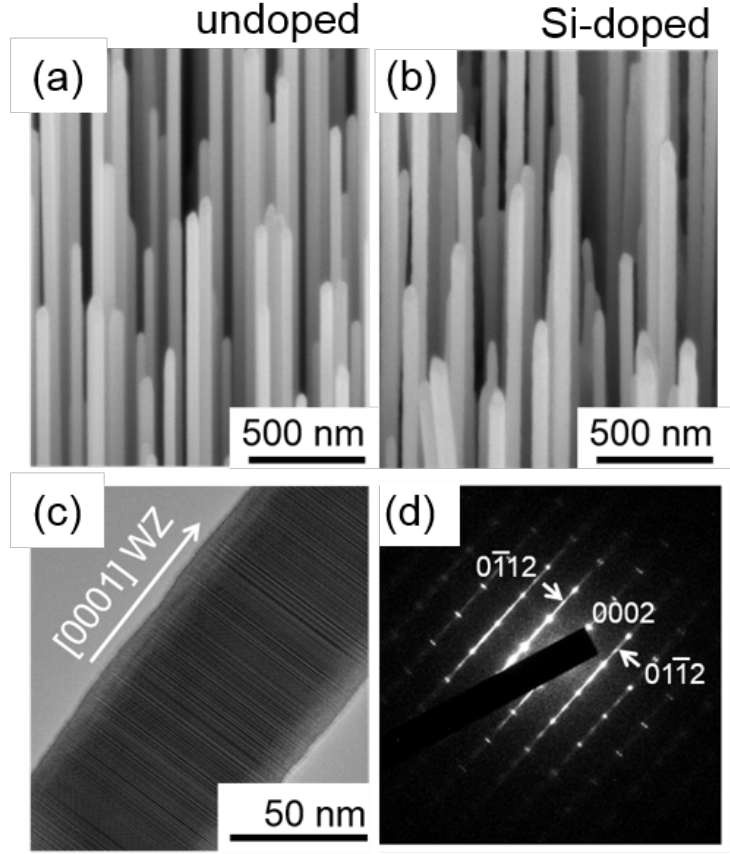


Figure 3.1. SEM micrographs of (a) undoped InAs nanowires, and (b) Si-doped InAs nanowires (Si: 13 Å) as grown on Si (111), exhibiting similar morphologies. The TEM micrograph in (c) and corresponding SAD pattern (d) recorded from a Si-doped InAs nanowire (Si: 13 Å) illustrate a WZ-dominated crystal phase with many stacking along the [0001] nanowire growth direction.

concentrations of $2.1 \cdot 10^{18} \text{ cm}^{-3}$ (11A), $6 \cdot 10^{18} \text{ cm}^{-3}$ (12A) and $1.4 \cdot 10^{19} \text{ cm}^{-3}$ (13A) for thin (100)-oriented films grown at a growth rate of $1 \text{ } \mu\text{m/h}$. For reference, the nanowires in the present study grow ~ 1.5 -2 times faster.

Interestingly, the aspect ratio and morphology of the Si-doped InAs nanowires remains largely unchanged with respect to undoped InAs nanowires (see Fig. 3.1), independent of the supplied Si dopant flux. On average, the 90-min long growths resulted in ~ 2.3 – $3.4 \text{ } \mu\text{m}$ long nanowires with diameters in between ~ 60 – 110 nm for each of the four investigated nanowire samples, as evaluated from a statistical

analysis of at least 20 nanowires/sample using SEM imaging. Any changes in growth dynamics due to the presence of Si doping are therefore smaller than the statistical dispersion of nanowire lengths and diameters within a given sample. Since this dispersion is relatively large in nanowires nucleated from random pinholes, we also examined the growth kinetics in high-uniformity periodical nanowire arrays on lithographically prepatterned $\text{SiO}_2/\text{Si}(111)$ substrates as reported elsewhere [317]. Although the length and diameter dispersion is substantially reduced in this control experiment, no marked change in the aspect ratios and morphologies was observed upon Si doping. This observation differs markedly from previous findings of both MOCVD- (metal organic chemical vapor deposition) [311, 314] and MBE-grown [315] catalyst-free InAs nanowires. Wirths et al. [314] and Dimakis et al. [315] observed a continuous decrease (increase) in nanowire length (diameter) with Si doping, irrespective of the different surface chemistries of the employed dopants (Si_2H_6 in MOCVD vs. atomic Si in MBE). In contrast, Ghoneim et al. [311] found that a change in aspect ratio of Si-doped InAs nanowires (along with a deterioration of morphology) occurs only for very high Si dopant fluxes, corresponding to active dopant concentrations $> 5 \cdot 10^{19} \text{ cm}^{-3}$. Hence, the dopant fluxes used in the present study appear insufficient to induce drastic morphological changes. Transmission electron microscopy (TEM) was performed on individual nanowires transferred onto carbon-coated grids to identify the crystal phase and defect structure of the undoped and Si-doped InAs nanowires. Based on an analysis of multiple nanowires per sample, we found that the nanowires crystallize preferentially in the WZ phase and exhibit a high density of stacking defects, similar to our previous findings of undoped InAs nanowires [22, 90]. A representative TEM micrograph along with the respective selected area diffraction (SAD) pattern are shown in Figs. 1(c,d) for nanowires grown under the highest Si dopant flux (13A). From the SAD pattern distinct WZ-sensitive reflections (i.e., $01\bar{1}2$ and $0\bar{1}12$) are clearly visible, while the streaks between individual reflections indicate the high stacking disorder along the $[0001]$ growth direction [90]. Since no qualitative differences are found between undoped and Si-doped InAs nanowires, the microstructure of non-catalytic InAs nanowires is insensitive to Si doping under the given growth conditions. This is in good agreement with other Si-doping studies of InAs nanowires reported in the literature [314, 315].

3.3.2. Estimating carrier concentration via Seebeck and NW-FET measurements

To identify the effect of the different Si dopant fluxes on the active carrier concentration, Seebeck effect measurements were conducted at room-temperature. Thermoelectric device structures were fabricated from single nanowires dispersed onto 200 nm $\text{SiO}_2/\text{n}^+\text{-Si}$ substrates using electron beam lithography, metal evaporation and lift-off. As shown in Fig. 3.2(a), the devices consist of an InAs nanowire with two Ni (nickel) contacts on each end that serve as probes for temperature (resistive thermometers) and Seebeck voltage. To induce a Seebeck voltage across a single nanowire, a temperature gradient was established by resistively heating one end of the nanowire using a meandering metal strip line consisting of five parallel 22- μm long, 1- μm wide and 100-nm thick strips of Ni [318]. This generates a temperature gradient of a few Kelvin that was measured in a four-terminal sensing geometry, i.e., the first resistive thermometer was biased via contacts 1 and 2 and the voltage drop was measured across contacts 3 and 4. For the second thermometer, contacts 5 and 6 were biased and 7 and 8 were used for sensing. The resulting Seebeck voltage was measured between one of the blue-colored (cold) and one of the red-colored (hot) contacts, e.g. between contacts 8 and 3. Measurements were performed on chip-carriers connected to a 3×8 switching matrix, which was purged with N_2 gas to ensure low humidity at a constant temperature. Two constant current supplies (Yokogawa 7651) were used to connect to the resistive heater and thermometer, respectively, while a differential voltage amplifier (Femto DLPVA-100FD) together with a Keithley 2000 multimeter were employed to probe both the Seebeck voltage and voltage drops over the thermometers. Fig. 3.2(b) shows the Seebeck voltage as a function of temperature difference (0-2 K) for representative devices fabricated from undoped and Si-doped InAs nanowires. Note that the plotted Seebeck voltage data is already corrected by subtraction of the respective Seebeck voltage induced by the Ni contacts (Seebeck coefficient $S_{\text{Ni}} = -19 \mu\text{V/K}$ [318]). The Seebeck voltage V varies linearly with the measured temperature difference ΔT , with the slope giving directly the Seebeck coefficient of the InAs nanowires. As expected, all investigated nanowires exhibit a negative slope indicative of n-type conduction. While the Seebeck coefficient of the undoped InAs nanowire is as high as $-352 \mu\text{V/K}$, its magnitude decreases for the Si-doped InAs nanowires, yielding $S = -62 \mu\text{V/K}$ for the lowest doped sample (11 Å), $S = -46 \mu\text{V/K}$ for the medium doped sample (12 Å), and $S = -38 \mu\text{V/K}$ for the highest doped sample (13 Å) (see

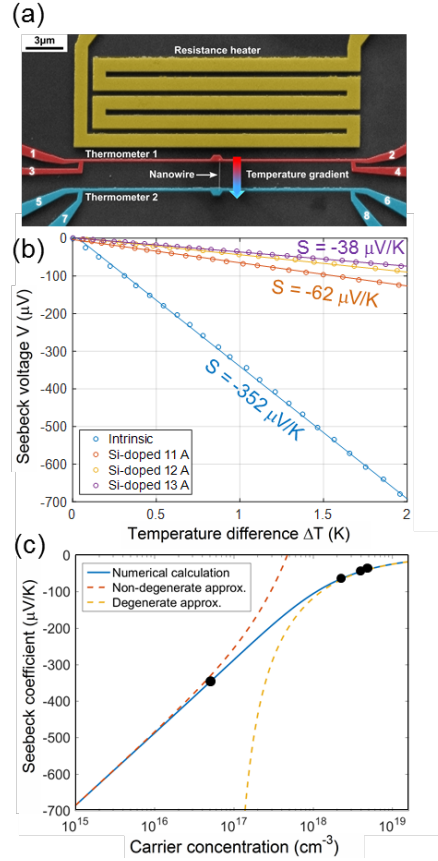


Figure 3.2. (a) Color-coded SEM image of a typical single nanowire device for Seebeck effect measurements containing lithographically defined resistive heater and thermometers at both nanowire ends; (b) Seebeck voltage versus applied temperature gradient at room-temperature as obtained from three Si-doped InAs nanowires with different dopant fluxes (11A, 12A, 13A) in comparison with an undoped InAs nanowire. The Seebeck coefficients are extracted from linear fits to the data; (c) Calculated Seebeck coefficient of n-type InAs as a function of carrier concentration; the blue curve is numerically calculated, while the red and yellow curves are analytical approximations for the non-degenerate and degenerate case, respectively. Experimental data points as obtained from (b) are also plotted (black symbols), with corresponding carrier concentrations ranging from $\sim 5 \cdot 10^{16} \text{ cm}^{-3}$ (undoped InAs nanowires) to $2\text{-}5 \cdot 10^{18} \text{ cm}^{-3}$ (doped InAs nanowires).

also Table 1). The relatively small change in Seebeck coefficient among the three Si-doped InAs nanowire samples suggests that the free carrier concentration does not change significantly with increasing Si flux beyond 11 A.

To verify this, we calculated the dependence of the Seebeck coefficient on n-type carrier concentration by solving the electronic part of the Boltzmann transport equation according to Ref. 284 (see also Supporting Information). Using a lattice temperature of 300 K, an electron effective mass of $m^*/m_0 = 0.023$, a unity scattering parameter [284], and assuming bulk-like electronic properties (no 1D electron density of states – DOS), we derived a numerical solution as plotted on Fig. 3.2(c) by the blue curve. The assumption of bulk-like electronic DOS is fully valid here, since the diameters of our investigated nanowires are well above the dimensions for 1D-quantum confinement [22]. We further note that our numerically calculated data agrees well with experimental data obtained for bulk InAs at room-temperature [319]. For comparison, we also plotted analytical solutions for the degenerate and non-degenerate conduction cases, which are approximations based on the assumption of parabolic band dispersion [284]. In order to get a direct estimate of the carrier concentration of the investigated InAs nanowires, we plotted the as-measured Seebeck coefficients onto the numerically calculated Seebeck coefficient data. From this we find that the undoped InAs nanowire has a carrier concentration of $\sim 5 \cdot 10^{16} \text{ cm}^{-3}$, whereas the Si-doped InAs nanowires exhibit carrier concentrations of $\sim 2\text{-}5 \cdot 10^{18} \text{ cm}^{-3}$. A statistical analysis of the range of carrier concentrations obtained from several nanowires per sample is further presented in Table 1 and shown in Fig. 3.6. Two important messages can be derived from the extracted carrier concentration dependency. First, our undoped nanowires reveal some of the lowest free carrier concentrations ever measured in intrinsic InAs nanowires, which is likely a result of the pure MBE growth environment. MOCVD-grown InAs nanowires have carrier concentrations typically 1-2 orders of magnitude larger [318, 320, 321]. Secondly, the free carrier concentration for the Si-doped InAs nanowires saturates quickly in the low- to mid- 10^{18} cm^{-3} range, despite the increasing Si dopant flux. This behavior suggests either strong carrier compensation effects or a significant dopant incorporation limit under high Si doping conditions.

To further confirm this trend, we have also conducted NW-FET measurements on single nanowire devices to allow an independent estimation of the carrier concentration. Back-gated NW-FETs were fabricated using a similar device geometry as for the Seebeck effect measurements. The NW-FET devices consisted of individual InAs nanowires drop-cast directly on 200-nm $\text{SiO}_2/\text{n}^+\text{-Si}$ (i.e., global back gate) and contacted by four Ni/Au Ohmic contacts to realize 4-terminal (4T) transport measurements. Further

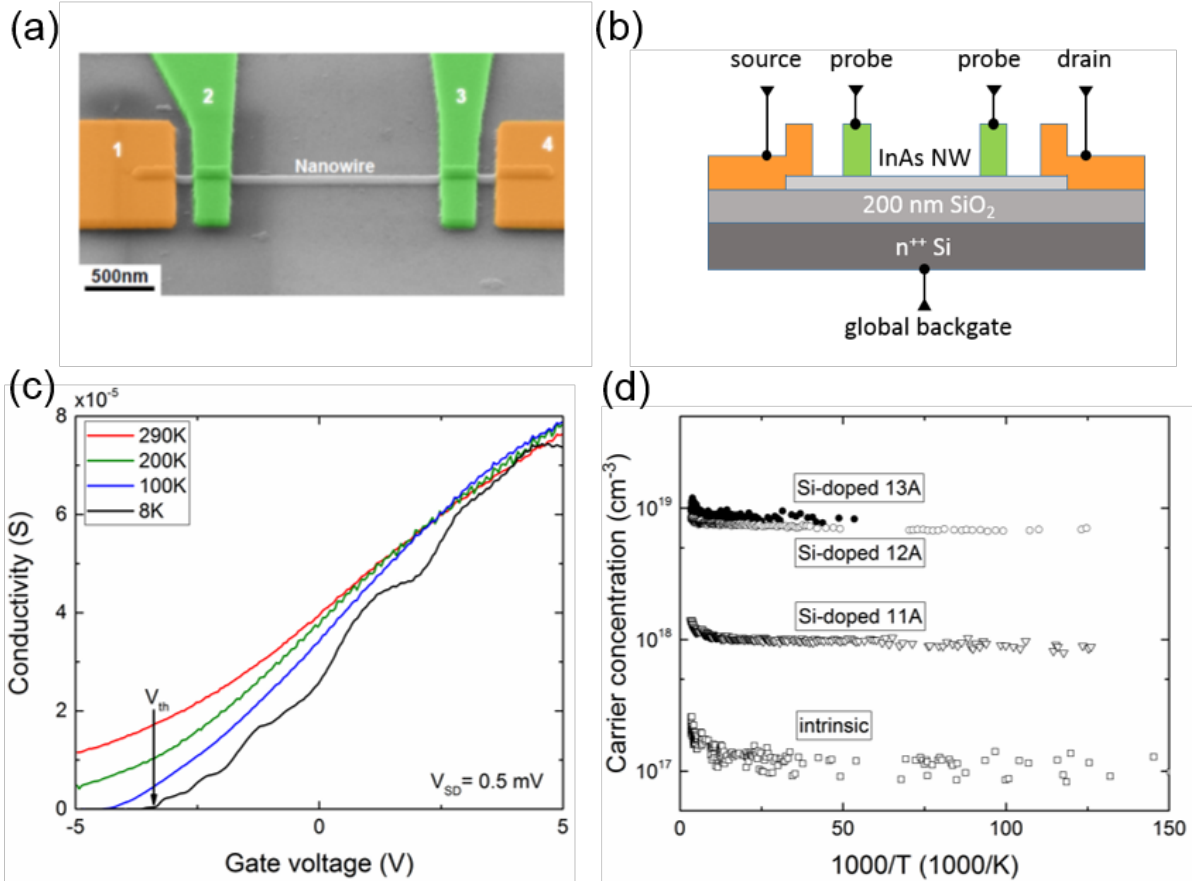


Figure 3.3. (a) Color-coded SEM image and (b) schematic illustration of a typical 4-terminal InAs NW-FET, consisting of four Ohmic contacts (outer contacts for source and drain and inner probe contacts). The n⁺⁺-Si substrate serves as a global backgate. (c) Transfer characteristics (conductivity versus gate voltage) as obtained from an intrinsically undoped InAs NW-FET at different measurement temperatures using a source-drain voltage of $V_{SD} = 0.5$ mV. The threshold voltage V_{th} at pinch-off is used to extract the carrier concentration. (d) Inverse temperature dependence of the carrier concentration of four representative InAs nanowires under different doping conditions.

details about device fabrication and contact formation are reported elsewhere [322]. An SEM image along with a schematic illustration of a typical four terminal NW-FET device is shown in Figs. 3(a,b). The 4T-device geometry allows us to separate intrinsic nanowire conductivity from nanowire contact resistance. This was achieved by applying a dc voltage (V_{SD}) to an outer contact and measuring the respective current between the outer source and drain contacts (1,4), whereas the voltage drop due to the intrinsic nanowire conductivity was measured via the inner probe contacts (2,3). Temperature-dependent 4T-measurements

Table 3.1. Summarized data of the undoped and three Si-doped InAs nanowire samples grown under three different Si dopant currents with corresponding nominal Si dopant concentrations calibrated on planar films (at 1 $\mu\text{m/hr}$ growth rate); the APT data gives the measured Si dopant concentration in the bulk region of the nanowire (accuracy of $\pm 5 \cdot 10^{17} \text{ cm}^{-3}$) for 1-2 nanowires measured per samples; the typical range of Seebeck coefficients S (absolute values) and n-type carrier concentrations from Seebeck effect and NW-FET measurements at room-temperature are listed for comparison (measured on 2-6 nanowires/sample); μ is the corresponding field effect mobility extracted from the NW-FET transconductance at room-temperature.

Si flux (A)	nom. [Si] (cm^{-3})	bulk [Si] (APT) (cm^{-3})	S ($\mu\text{V/K}$)	n (Seebeck) (cm^{-3})	n (NW-FET) (cm^{-3})	μFE (cm^2/Vs)
0	-	-	299-352	$4.0-8.7 \cdot 10^{16}$	$1.0-1.2 \cdot 10^{17}$	1205 (± 70)
11	$2.1 \cdot 10^{18}$	$1.5 \cdot 10^{18}, 5 \cdot 10^{18}$	41-62	$2.5-4.6 \cdot 10^{18}$	$1.0-4.0 \cdot 10^{18}$	542 (± 114)
12	$6.0 \cdot 10^{18}$	$1.8 \cdot 10^{18}, 2.5 \cdot 10^{18}$	44-104	$1.0-4.1 \cdot 10^{18}$	$6.8-10 \cdot 10^{18}$	406 (± 75)
13	$1.4 \cdot 10^{19}$	$4.3 \cdot 10^{18}$	38-49	$3.4-5.3 \cdot 10^{18}$	$0.7-3.6 \cdot 10^{19}$	243 (± 133)

were performed between 6 K and 290 K in a He-4 flow cryostat where the NW-FET samples were placed on custom-made chip carriers using wire bonding. Representative T-dependent transfer characteristics of the intrinsic nanowire conductivity σ are shown in Fig. 3.3(c) for the case of an undoped InAs nanowire using a source-drain voltage of $V_{SD} = 0.5 \text{ mV}$. As expected, intrinsic n-type carrier conduction is confirmed by the increase in conductivity with increasing positive V_G . At low temperature (e.g. 8K) we also observe step-like pinch-off characteristics, which may be due to the depopulation of individual subbands as previously noted for e.g. InAs- and GaAs-based NW-FETs [323, 324]. Note that the pinch-off and the respective threshold voltage V_{th} shift to increasingly negative V_G with rising temperature. From the threshold voltage V_{th} , which is derived from a linear regression of $\sigma = g_m \cdot (V_G - V_{th})$ (g_m , transconductance), we can directly extract the carrier concentration n using $C_G \cdot V_{th} / (e \cdot l \cdot A)$ [322]. Here, C_G is the gate capacitance, which is estimated based on the widely used metal plate capacitor model of Ref. 325, while l and A are the length and cross-section area of the nanowire channel as measured by atomic force microscopy.

Fig. 3.3(d) compares the calculated carrier concentration as a function of inverse temperature for the undoped, intrinsic nanowire and typical nanowires from the three Si-doped samples analyzed in the same way. Additional data obtained from several other nanowires for each sample are further illustrated in Fig. 3.6 and Table 1, listing also values for the field effect mobilities that were extracted from the

transconductance, i.e., $\mu = g_m \cdot l^2 / (C_G \cdot V_{SD})$. For all investigated nanowires, the carrier concentration is fairly constant over the measured temperature range indicating the overall degenerate nature of both the undoped and Si-doped InAs nanowires. Only a marginal increase in carrier concentration may be noticed for temperatures above ~ 60 K, best illustrated for the undoped InAs nanowire. This behavior is likely due to a weak activation process from traps caused either by stacking defects or surface-related defect states [322]. Most importantly, as in the Seebeck effect measurements we observe a similar trend in the increase and saturation of carrier concentration with Si doping. However, compared to the Seebeck effect data the carrier concentrations extracted from the NW-FET measurements are on average higher (up to factor of 2-3 depending on sample) (see also Fig. 3.6). We suggest two reasons for this observation: First, the metal plate capacitor model used to derive the gate capacitance [325] slightly overestimates the capacitance and, thus, the charge carrier concentration by ~ 10 -20%. Secondly, and more significantly, field-effect measurements are very sensitive to spatially fixed surface/interface charges that occupy the surface and interface states between the nanowire surface and metal gate. These states cause Fermi level pinning at the nanowire surface [326] and trap additional charges induced by the applied gate voltage [327]. As a result, only a fraction of the induced charge contributes free carriers to the nanowire channel, which in turn yields to an overestimation of the free carrier concentration. Moreover, we observe that the deviation in carrier concentration between NW-FET and Seebeck effect data is more significant for increased Si dopant fluxes, with estimated field-effect concentrations exceeding 10^{19} cm^{-3} for the highest doped sample. This suggests that excess Si dopants may accumulate in the near surface region of the nanowire-channel and modify the Fermi level pinning, which is sensitively probed by the NW-FET measurements. This hypothesis is further examined below by APT measurements of the Si dopant distribution across individual nanowires. Moreover, we found that along with the evolution of carrier concentration upon doping, the field-effect mobility decreases significantly, i.e., from $\sim 1200 \text{ cm}^2/\text{Vs}$ (undoped nanowires) to $\sim 540 \text{ cm}^2/\text{Vs}$ and below (Si-doped nanowires) at room temperature (see also Supporting Information). This behavior mimics closely the mobility versus n-type doping dependence of bulk InAs [328] as observed also in previous investigations of MOCVD-grown Si-doped InAs nanowires [311].

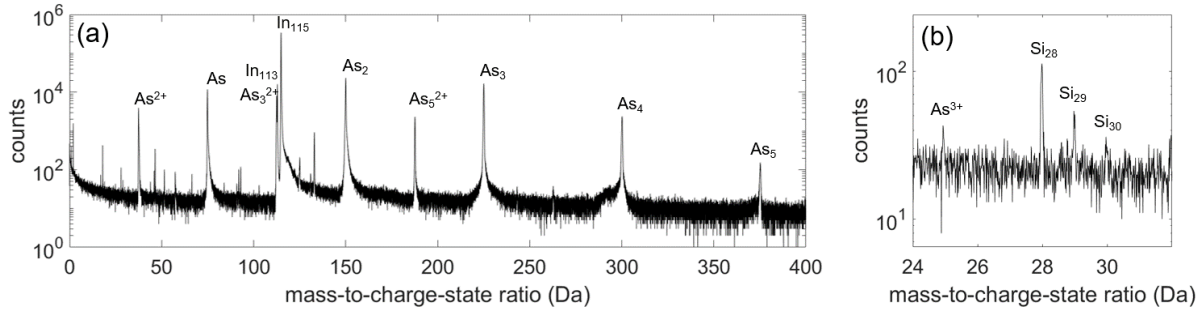


Figure 3.4. (a) Typical APT mass spectra for “bulk” region of InAs nanowire. (b) Mass Spectrum from 24-32 Da to show Si peaks.

3.3.3. Atom probe tomography for mapping Si dopants

To further explain the characteristic saturation behavior in carrier concentration with increasing Si doping, we performed APT on selected Si-doped InAs nanowires to directly compare chemical with electrically active dopant concentrations. APT specimens were prepared by picking and Pt welding individual nanowires onto tungsten probe tips using a nanomanipulator in vacuum. Further details of the specimen preparation can be found in Appendix A and elsewhere [329]. APT analysis was performed by LEAP 4000X Si under the following conditions: 0.1-0.4 pJ laser energy, 250 kHz pulse rate, 30K stage temperature, and 0.5% detection rate. Figure 3.4 shows a typical mass spectra recorded from a cylindrical ROI in the center of the nanowire (excluding the surface oxide). The peaks from Si dopants can be seen in 3.4(b) at 28, 29, and 30 Da. Some spectra showed higher Si_{29} and Si_{30} peaks than the expected isotope percentage of 4.69% and 3.09% for Si_{29} and Si_{30} respectively, when comparing them to the peak at 28 Da. To avoid contributions from other molecular species, only Si_{28} , Si_{28}^{2+} , Si-O, and Si-As were include in Si concentration and error analysis. Si concentrations were calculated from APT runs at 0.1 pJ laser energy, as we empirically determined that the measured concentration did not vary with laser pulse energy about this point. However, contour maps of the Si dopant species on the outside of the nanowire, as shown in Figure 3.5(a,b), were taken from APT runs at higher laser energies (0.4 pJ), because the change in tip curvature brought the heavily doped region on the outside of the nanowire into the field of view at this laser energy. Details on this analysis can be found in Appendix A.

A representative map of the Si dopant distribution across a single nanowire is illustrated in Fig. 3.5(a) for the highest doped sample (Si: 13 Å). Similar dopant distribution maps were also recorded from nanowires with lower Si doping and are shown in the Supporting Information of Reference [322]. Clearly, we observe an overall homogeneous distribution of Si dopants inside the nanowire, but a distinctly higher Si concentration near the nanowire surface. Note that the contrast facilitated by the enriched Si layer reproduces closely the hexagonal nanowire geometry, however, the enrichment is visible only along one side of the nanowire due to the limited field of view in APT for specimens that are not perfectly vertically oriented on the probe tip. Due to the limited field of view, it is therefore helpful to probe also the presence of oxygen (O) impurities arising from the inherent surface oxide layer on the $\{2\bar{1}10\}$ InAs nanowire sidewalls [327] and thereby delineate the exact position of the nanowire surface (Figure 3.5(b)). We note that the O content is reported for comparison, but the concentration should not be taken as quantitative at the very edge of the reconstruction. We observe direct coincidence between the positions of the surface oxide layer and the enriched Si dopant layer, which is also illustrated by the proximity histogram plotted in Figure 3.5(c). The proximity histogram shows the Si dopant and O impurity distribution together with the measured molar fraction of InAs when moving from center to surface of the nanowire along one of the $\langle 2\bar{1}10 \rangle$ directions. The average Si dopant concentration in the bulk part of the nanowire was determined to be $\sim 4.3 \times 10^{18} \text{ cm}^{-3}$, while it increases by at least 2 orders of magnitude at the surface. A similar behavior was also observed for nanowires measured from samples with lower Si dopant cell fluxes (see Supporting Information of Reference 322). The fact that the enriched Si layer is confined within the surface oxide suggests that only minimal carriers would be activated from this highly doped region and that the free carrier concentration is determined by the Si dopant concentration in the bulk part of the nanowire.

Indeed, this correlation can be directly seen when comparing the Si dopant concentrations in the bulk of the nanowire (APT data) with the activated bulk carrier concentrations extracted from Seebeck effect measurements as shown in Fig. 3.6. The results clearly show that the active carrier concentration matches well with the physical dopant concentration in the center of the nanowire within the experimental error for each of the three investigated Si-doped InAs nanowire samples. This means that carrier compensation

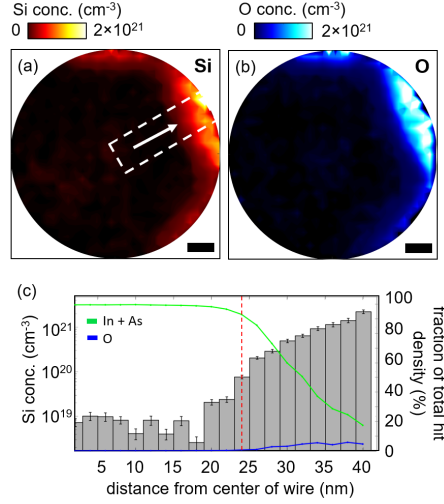


Figure 3.5. APT reconstruction of a Si-doped InAs nanowire (13A) shown as projected 2D compositions maps of (a) silicon (Si) and (b) oxygen (O). The full nanowire cross-section is not visible in the reconstruction, but the location of the InAs-native oxide interface is identified by the increase in O. Enrichment of Si is found at the nanowire surface. Scale bars are 10 nm. (c) Corresponding 1D composition profile moving from the nanowire center to the surface along one of the major $\{2\bar{1}10\}$ directions (white box in (a)). The red dashed line indicates the approximate location of the interface with the native oxide. Along one side of the nanowire due to the limited field of view in APT for specimens that are not perfectly vertically oriented on the probe tip. Due to the limited field of view it is therefore helpful to probe also the presence of oxygen (O) impurities arising from the inherent surface oxide layer on the $\{2\bar{1}10\}$ InAs nanowire sidewalls [327] and thereby delineate the exact position of the nanowire surface (Fig. 3.5(b)). We note that the O content is reported for comparison but the concentration should not be taken as quantitative at the very edge of the reconstruction. We observe direct coincidence between the positions of the surface oxide layer and the enriched Si dopant layer, which is also illustrated by the proximity histogram plotted in Fig. 3.5(c). The proximity histogram shows the Si dopant and O impurity distribution together with the measured molar fraction of InAs when moving from center to surface of the nanowire along one of the $\{2\bar{1}10\}$ directions. The average Si dopant concentration in the bulk part of the nanowire was determined to be $\sim 4.3 \cdot 10^{18} \text{ cm}^{-3}$, while it increases by at least one order of magnitude at the surface. A similar behavior was also observed for nanowires measured from samples with lower Si dopant cell fluxes (see Supporting Information). The fact that the enriched Si layer is confined within the surface oxide suggests that only minimal carriers would be activated from this highly doped region and that the free carrier concentration is determined by the Si dopant concentration in the bulk part of the nanowire.

effects are negligible for the range of Si dopant concentrations explored here. Fig. 3.6 also plots the respective carrier concentrations estimated from NW-FET measurements. The fact that these are higher

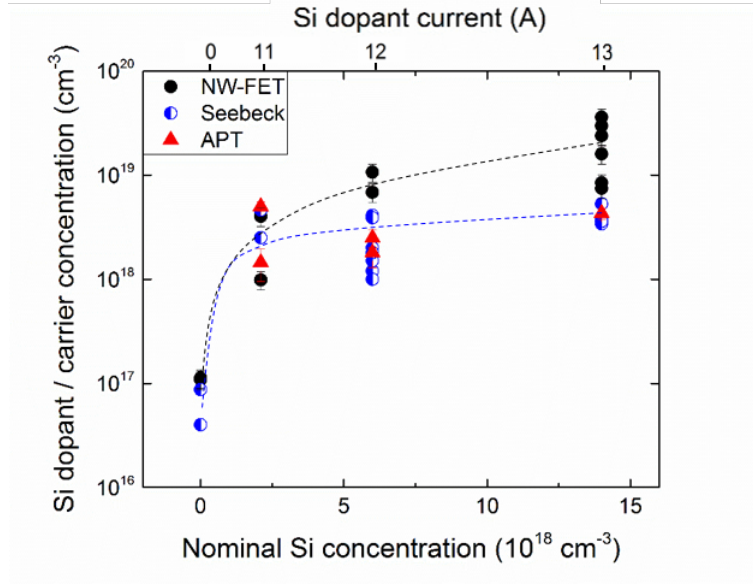


Figure 3.6. Statistical distribution of the concentrations of bulk Si dopants (APT data) and n-type charge carriers (Seebeck and NW-FET data) as a function of nominal Si concentration (Si dopant current) at room-temperature. The blue and black dashed curves are guides to the eye describing the evolution of Seebeck and NW-FET data, respectively. The data points shown here are also summarized in Table 1.

than the physical dopant concentration within the nanowire (especially for high dopant fluxes) confirms that the NW-FET measurements are impacted by surface/interface effects and the presence of the enriched Si layer. We speculate that the Si-rich surface layer may increase the downward band bending at the nanowire surface, similar to observations in e.g. sulfur-passivated InAs nanowire [330], thus leading to larger trap state densities which obscure the free carrier concentration. A fully quantitative correlation between the excess Si accumulation in the surface oxide and active carriers within the surface layer is, however, difficult, due to the presence of other donor-type surface state defects [326] and the fact that the Si enrichment is not homogeneous across the surface region. To resolve this, systematic X-ray photoelectron spectroscopy (XPS) experiments need to be performed to directly correlate the modified core level spectra arising from the Si enrichment and the induced changes in respective surface band bending.

To finally discuss the origin of the excess Si accumulation on the WZ- $\{2\bar{1}10\}$ InAs nanowire surfaces and the observed dopant incorporation limit in the nanowires, a few kinetic and thermodynamic

considerations can be undertaken. First of all, the underlying non-catalytic vapor-solid (VS) growth mode implies that the majority of Si dopant incorporation occurs via the sidewall facets, since on slow growing facets dopant incorporation rates are generally enhanced compared to fast growing facets [331]. This behavior assumes a unity sticking coefficient of Si and a very low Si surface diffusion, irrespective of the given facet, just as in planar III-V semiconductor films [332, 62]. Notably, in planar III-V based films precipitation of Si at the growth surface has also been found under high Si dopant fluxes, limiting the incorporation of Si to concentrations below the $\sim \text{mid-}10^{18} \text{cm}^{-3}$ range [333]. It has been speculated that such Si-rich phases reduce the As coverage at the growth surface, inducing changes in the dynamic surface structure, i.e., surface reconstructions and surface strain, which may inhibit effective dopant incorporation [334]. Such saturated dopant-rich phases at the surface of growing layers have also been found in other III-V systems where the dopant incorporation becomes independent of the dopant arrival rate [335]. To further examine the link between segregated phases and associated modifications of the surface structure in the present InAs nanowires requires additional studies, such as scanning tunneling microscopy along with theoretical modeling. Finally, we wish to emphasize that dopant segregation to the lateral sidewall surfaces of nanowires seems to be also explained by recent first principles calculations of the segregation energies of various different dopants in III-V based nanowires [336]. In the framework of these calculations the segregation effects were also predicted for Si-doped InAs nanowires, where dopant atoms prefer to substitute for surface atoms with extra dangling bonds or may be trapped at subsurface sites close to atoms with additional dangling bonds.

3.4. Summary

In summary, we demonstrated a direct correlation between the chemical and electrically active dopant concentrations in Si-doped InAs nanowires grown in a completely catalyst-free growth mode. By employing atom probe tomography, Seebeck effect measurements and NW-FET characterization we found a characteristic dopant incorporation limit at concentrations around $\text{mid-}10^{18} \text{cm}^{-3}$. Up to these dopant concentrations the free carrier concentration follows nicely the Si dopant densities incorporated in the bulk of the nanowire, confirming that compensation effects are negligible. For comparison, undoped InAs

nanowires exhibit free carrier concentrations of $\sim 5 \cdot 10^{16} - 1 \cdot 10^{17} \text{ cm}^{-3}$ which are among the lowest ever reported values for n-type InAs nanowires. The results reveal also that under the employed growth and Si doping conditions a thin layer of segregated Si forms on the nanowire sidewall surfaces with concentrations of $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$, which confirms recent first-principles calculations of the segregation energies of doped III-V nanowires.

CHAPTER 4

3D Ptychography for Strain Mapping in Extended Objects

This chapter, excluding Section 4.4, was reprinted with permission from M.O. Hill, et al. “Measuring three-dimensional strain and structural defects in a single InGaAs nanowire using coherent X-ray multi-angle Bragg projection ptychography” *Nano Letters* 18.2, (2018): 811-819. Copyright © 2018 American Chemical Society.

4.1. Motivation for Research

Nonplanar semiconductor heterostructures provide opportunities for novel and efficient functionality over a broad range of applications. For example, ternary III-As nanowire heterostructures are promising near-IR emitter/detectors for applications including on-chip photonic information transfer due to their bandgap tunability and high electron mobility [337, 338, 339, 340]. Additionally the nanowire geometry enables direct integration of III-V's onto silicon, as the small interface area mitigates the formation of dislocations and anti-phase domain boundaries [341, 98, 342]. However, III-As nanowires commonly exhibit nanoscale structural inhomogeneities such as stacking faults, polytype insertions, and nanofaceting [78, 77]. In addition, composition fluctuations in ternary alloys and the resulting lattice strain can modify the electronic bandgap [58, 343, 78]. When nanoscale defects occur together with composition and strain variations on multiple lengthscales, it can be challenging to establish the physical origins of properties and device behaviors that are probed over microscale volumes. Therefore, the necessary optimization of nanowire materials for specific electronic and optoelectronic devices will require improved approaches to map local inhomogeneities in crystal structure and composition throughout a nanowire, preferably using approaches that enable *in operando* analysis.

Although the present work includes analysis of previously unreported perturbations in nanowire structure encompassing nanometer to micron lengthscales, we are especially motivated to probe structural

features that strongly influence optical emission and electronic transport properties. In particular, there is a strong correlation between the density of stacking defects and mobility in III-As nanowires. [185, 324] Comparing high resolution transmission electron microscopy (TEM) images of free standing nanowires with position dependent field effect mobility measurements on InAs nanowire devices, Schroer et al [185] showed that low densities of stacking faults localize electrons, leading to transport characteristics consistent with quantum dot formation even in devices with low resistance Ohmic contacts. Irber et al [324] later showed that diffusive quantum transport in quasi 1-D sub-bands can be observed in modulation doped GaAs nanowires even in the presence of stacking faults, but as the stacking fault density increases, quantum features are washed out due to increased scattering. It is also well established that crystal phase switching between wurtzite (WZ) and zinc blende (ZB) polytypes, which exhibit a type II band alignment, [344] leads to the formation of quantum dots that act as single photon emitters. [95] Further, Jahn et al [344] observed that GaAs nanowires with the same average WZ/ZB content may luminesce above or below the ZB bandgap, dependent on the thickness of the ZB insertions. The interpretations advanced in the works cited above require *a priori* knowledge of the spatial variation in the density of stacking defects. Methods such as transmission electron microscopy have contributed greatly to our understanding of structure/property relationships in nanowires, and the development of complimentary approaches compatible with more complex sample environments (*e.g.* nanowire devices fabricated on standard Si wafers) is needed to deepen our understanding.

A promising avenue lies in coherent x-ray diffraction imaging (CDI), which offers the advantage of probing strain and other structural features in nanowires over a larger field of view on thicker substrates and embedded in operating devices. To date, 2D CDI methods have been used to view longitudinal projections [240] or cross-sectional cuts [345, 346, 347] of lattice strain in III-V nanowires. However, scaling the approach to three dimensions and towards multi-scale imaging is not straightforward because high resolution in 3D is needed of a high-aspect-ratio sample. Existing 3D CDI techniques are not well suited for measuring extended structures such as nanowires that are larger than the x-ray beam footprint. Further, abruptly varying features, such as crystal phase switching at few-nanometers length scales in nanowires, cannot be reliably imaged using traditional CDI methods [348, 349].

Here we overcome the limitations of conventional 3D CDI by adapting Bragg ptychography, a variant of CDI based on scanning focused coherent x-ray beam measurements, to robustly reconstruct 3D images of strain and stacking defects in single InGaAs nanowires. The analysis focuses on InGaAs nanowires grown by catalyst-free molecular beam epitaxy (MBE) which have been shown to have wide compositional tunability and can be used as a foundation for epitaxial core-shell heterostructures[103, 350] for near-IR optoelectronics. We demonstrate reconstruction of single stacking defects and lattice strain in InGaAs nanowires on Si substrates with a spatial resolution better than 3 nm. To do so, we introduce an implementation of Bragg ptychography (named multi-angle Bragg Projection Ptychography, maBPP) in combination with coarse-scanning Bragg nanodiffraction analysis to provide a holistic view of the hierarchical structure of a single InGaAs nanowire spanning from nanometers to several microns. The methodological framework we present, and the proof of principle we demonstrate, can enable new insights into the impact of stacking faults and crystal phase switching on the characteristics of individual substrate-supported nanowire devices *in operando*.

4.2. Introduction to maBPP

Prior to describing the data and analysis, we briefly introduce 3D Bragg ptychography and the motivation for the specific advance in methodology that was required to resolve single stacking faults in a nanowire with a high density of these defects. We utilize 3D Bragg ptychography as it satisfies many attributes necessary for characterizing complex III-V nanowires: nanoscale resolution, sensitivity to different structural features, and the potential for mapping extended crystals. With Bragg ptychography, nanoscale variations in crystal structure can be imaged by numerically inverting coherent diffraction intensity patterns measured in the vicinity of a Bragg peak [242, 351]. The approach utilizes a localized scanning x-ray probe (typically focused with an x-ray optic) and entails measuring oversampled Bragg coherent diffraction patterns at different overlapping scan positions at one[242] or more[351] angles near the Bragg diffraction condition of an extended crystal. Gradient-based iterative inversion algorithms have been developed [352, 353, 354] to retrieve the phases (which cannot be measured experimentally) of the intensity patterns in such a data set and to provide a real-space image of the complex-valued structure

factor of the measured Bragg peak. Variation in the phase of these structure factor images can then be interpreted in terms of various phenomena, including lattice displacement from elastic strain fields [355], defects in atomic stacking order [214, 356], individual dislocations [357], and ferroelectric polarization [358]. Typically, these phenomena can be observed with a spatial resolution of 5-50 nm, depending on the signal-to-noise ratio (SNR) of the measurement and other factors such as scattering geometry, degree of probe overlap, and choice of reconstruction algorithm [354].

Traditional 3D Bragg ptychography utilizes data sets with fine angular steps about the Bragg peak (known as rocking curves) [351, 359], requiring that high SNR diffraction data be collected for all angles at each probe position. 3D reconstruction algorithms require that scan positions be commensurate at every diffraction angle to within a few percent of the beam diameter, a requirement that is highly challenging with state-of-the-art hard x-ray focusing optics that produce focii of <100 nm and operate in fly-scan mode [360, 361]. Alternatively, methods such as Bragg projection ptychography (BPP and 3DBPP) have been developed that only require a single angle measurement. Scanning Bragg nanodiffraction data at a single-angle can then be inverted into 2D [241] and 3D [242] images of lattice structure within a material. However, single-angle 3D BPP requires high diffraction angles ($>\sim 60^\circ$) that can be difficult to reach experimentally and at which Bragg peaks scatter more weakly.

We address these challenges by utilizing a generalized 3D multi-angle Bragg projection ptychography approach, which is described in more detail in the Algorithm Description section. maBPP relaxes experimental constraints such that a set of coherent diffraction intensity patterns measured at arbitrary angles and positions can be incorporated into a single 3D reconstruction, without requiring any position registration. Specifically, we implement maBPP by adapting the Ptychographic Iterative Engine (PIE) [352], a phase retrieval algorithm shown to be well suited for ptychographic imaging.

$\text{In}_{0.86}\text{Ga}_{0.14}\text{As}$ nanowires with diameters of 100-200 nm were grown by catalyst-free molecular beam epitaxy under conditions similar to those in Reference 362. Nanowires of this diameter range, and even larger diameters, are of interest for IR optoelectronics because optical modes are insufficiently confined at smaller diameters. [294] HRTEM investigation of similar samples revealed a primarily WZ crystal phase with a high density of stacking faults, typically spaced by <10 nm. No extended regions (>1 nm) of ZB

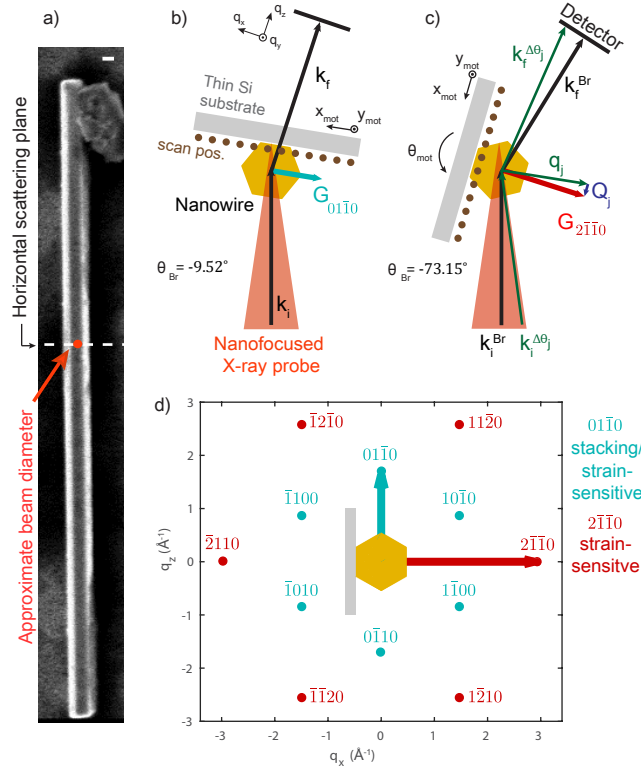


Figure 4.1. Experimental geometry at HXN beamline (a) SEM image of the investigated InGaAs nanowire. Scale bar is 100 nm. The focused x-ray probe (red circle) is approximately 50 nm in diameter. Scattering geometries used for the 0110 (b) and 2110 (c) conditions. θ_{Br} is the angle of the integrated intensity maximum of the rocking curve. k_i^{Br} and k_f^{Br} are the initial and final scattering vectors at θ_{Br} , defined by the momentum transfer vector G . $k_i^{\Delta\theta_j}$ and $k_f^{\Delta\theta_j}$ are the initial and final scattering vectors for the j th angle away from θ_{Br} , defined by the momentum transfer q_j , Q_{θ_j} away from G . (d) The reciprocal space lattice in the radial plane of the nanowire (cyan and red points) and a schematic of the facets of the InGaAs nanowire studied (yellow hexagon). The family of 2110 peaks of the WZ lattice correspond to the 202 family of peaks in the ZB structure, and they are sensitive to lattice strain fields within the nanowire. The 0110 peaks have no analog in the cubic ZB structure. These peaks are sensitive to stacking faults in the WZ phase as well as a component of lattice strain. Bragg ptychography nanodiffraction area raster scans were performed on the same nanowire at the 2110 and 0110 Bragg peaks and reconstructed into complementary 3D images.

were observed at these growth conditions [362]. To prepare a sample for structural imaging with maBPP, the nanowires were drop-casted onto a 10- μm -thick silicon substrate that transmits hard x-rays prepared for this application via selective etching and lithography by Norcada Inc., and the location of nanowires relative to chromium fiducial markers on the substrate was determined with scanning electron microscopy

(SEM), prior to x-ray investigations. The SEM characterization revealed that each nanowire was fixed to the substrate with an a -plane ($2\bar{1}\bar{1}0$) facet parallel to the Si surface. (We adopt hexagonal four-index notation in this work consistent with the hexagonal WZ crystal structure.) Figure 4.1(a) shows a SEM image of the 200-nm-diameter nanowire investigated.

Bragg ptychography coherent nanodiffraction measurements were performed at the Hard X-ray Nanoprobe (HXN) beamline of the National Synchrotron Light Source II (NSLS-II) [363, 364, 365]. A coherently-illuminated x-ray zoneplate with an outermost zone width of 40 nm was used to focus 10.4 keV monochromatic x-rays at the sample, forming a minimum spot size of 49 nm with an 80 mm focal length. The wavefront of the probe was characterized with standard direct-beam ptychography of a known reference sample [353] prior to the nanowire measurements. Scanning probe fluorescence measurements were used to locate an individual nanowire with the long axis aligned vertically. The vertical nanowire orientation enabled two different Bragg peaks ($01\bar{1}0$ and $2\bar{1}\bar{1}0$) to be accessed in the horizontal scattering plane, each sensitive to a different structural component of the nanowire. Figure 4.1(b-d) shows depictions of the scattering geometries used to reach the Bragg peaks measured here, as well as their reciprocal space orientation. At both Bragg conditions, 2D nanodiffraction maps were measured at a series of angles about the Bragg peak while simultaneously measuring Ga K-edge fluorescence.

Positional scans were done in a fly-scan mode, moving the sample with motors oriented parallel to the Si membrane surface (x_{mot} , y_{mot} in Figure 4.1(c)), and the angle was adjusted in 0.02° steps about the Bragg condition with a rotational stage (θ_{mot}) that rotated the nanowire along its long axes. Fly scans, now being increasingly utilized for ptychography measurements [360], were implemented with an average dwell time per scan point of 0.2 seconds in order to minimize scan time overhead and eliminate motor settling time. A Merlin pixel array detector was used with 512×512 square pixels with $55\mu\text{m}$ edges and a sample-to-detector distance of 500 mm and 330 mm for the $2\bar{1}\bar{1}0$ and $01\bar{1}0$ Bragg peak measurements respectively. These peaks were found at θ motor positions of $\theta_{Br}^{2\bar{1}\bar{1}0} = -9.52^\circ$ and $\theta_{Br}^{01\bar{1}0} = -73.15^\circ$, with the detector positioned 33.7° and 19.04° off the direct beam respectively, as shown in Figure 4.1. At each angle, about both Bragg peaks, overview nanodiffraction raster maps measured with coarse step sizes (~ 100 nm) were performed of the entire wire, which was used to correct for error from uncertainty in

the center of rotation of the θ motor. Then fine-stepped raster scans (step size ~ 25 nm) were used for Bragg ptychography data in specific regions of the wire. We note that we did not attempt to register probe scan positions as a function of angle, as this would be impractically difficult for a 50 nm beam. This emphasizes the need for the new maBPP approach, which allows for incommensurate positions to be incorporated into the phase retrieval.

The two Bragg peak measurements in this study were chosen to image different types of lattice structure in the InGaAs nanowires via the sensitivity of the Bragg structure factor. As illustrated in Figure 4.1(d), the family of $01\bar{1}0$ Bragg peaks originate only from the hexagonal WZ phase (this peak is forbidden in the cubic ZB structure). As has been derived previously [348, 366], the structure factor of a WZ $01\bar{1}0$ -type peak changes by $\pm 2\pi/3$ across a $\langle 0001 \rangle$ c -axis stacking fault. In addition to the spatial variations in structure factor from WZ stacking faults, any overall distortions of the crystal due to elastic strain, dislocations, etc. will also be encoded in the structure factor, and correspondingly in the phase of $01\bar{1}0$ Bragg ptychography reconstruction. The second Bragg peak belongs to the $(2\bar{1}\bar{1}0)$ family of WZ Bragg peaks which is not sensitive to WZ stacking faults, and is indistinguishable from the cubic ZB $(20\bar{2})$ type peaks. As a result, images derived from a $2\bar{1}\bar{1}0$ Bragg peak will reveal more subtle structural perturbations such as those due to elastic strain fields. In the remainder of the paper, we examine the qualitative differences between Bragg scattering patterns measured at the $2\bar{1}\bar{1}0$ and $01\bar{1}0$ Bragg peaks, show an analysis of $2\bar{1}\bar{1}0$ diffraction that reveals micron-scale structure in the nanowire, and conclude by discussing 3D images of nanoscale strain fields and stacking order obtained from maBPP reconstructions of both Bragg conditions.

The characteristics of typical scattering patterns measured at both Bragg conditions highlight their sensitivity to different local structure in the nanowire. Figure 4.2(a,b) shows rocking curves of the $2\bar{1}\bar{1}0$ and $01\bar{1}0$ Bragg peaks measured near the middle of the outlined regions in Figure 4.2(c). (The rocking curves were obtained by first registering the series of 2D overview nanodiffraction maps to one another using Ga fluorescence maps. The integrated-intensity rocking curves shown were then extracted from a fixed pixel position of the aligned nanowire fluorescence maps.) The coherent nanodiffraction patterns measured at the maxima of these rocking curves are inset in Figure 4.2. The diffraction pattern insets

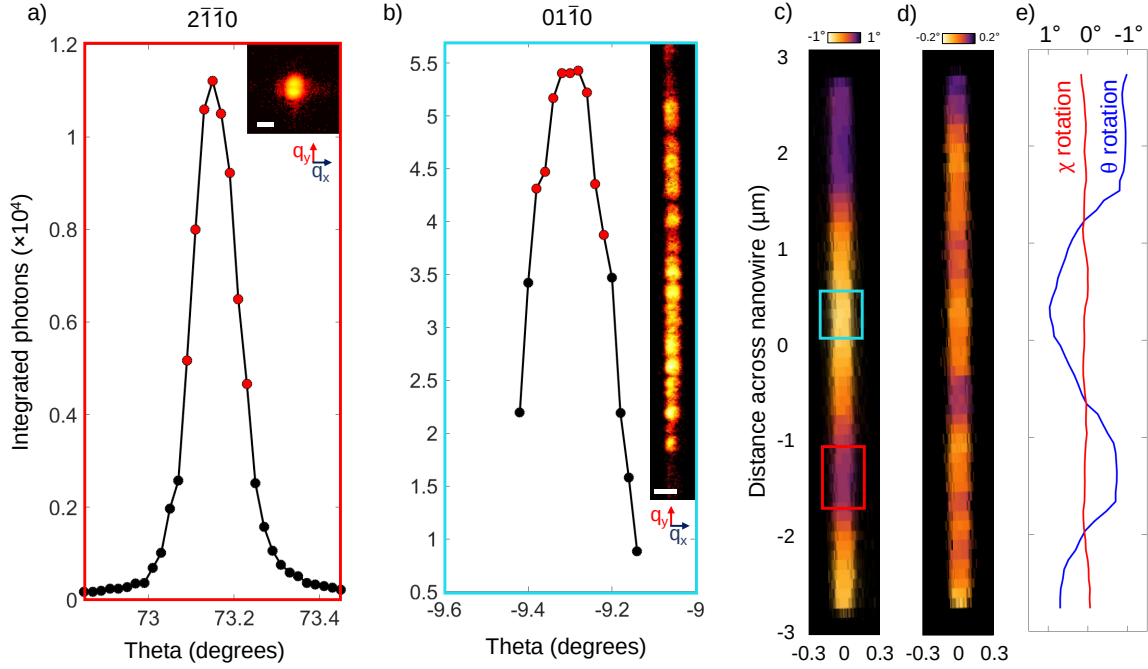


Figure 4.2. Sample rocking curves measured for the $2\bar{1}\bar{1}0$ (a) and $01\bar{1}0$ (b) peaks were taken taken from the center of red and cyan boxes in (c) respectively. Data was collected at each plotted point, but 3D maBPP reconstructions were performed in these regions using only the angles marked in red. Example 2D diffraction patterns (logarithmic intensity) at the Bragg maximum are shown in an inset. The diffraction pattern insets span different distances, with scale bars of 3 nm^{-1} (a) and 50 nm^{-1} (b). 2D diffraction peak mapping obtained from the $2\bar{1}\bar{1}0$ intensity patterns reveals a relative twist (c) about the long axis (about θ) and (d) a bending in the plane of the Si substrate (about χ) as a function of position across the nanowire. (e) 1D line cuts of twisting (blue) and bending (red) through the center of the nanowire. Variations in angle for (c),(d), and (e) are relative to their Bragg maximum near 73.15 degrees.

span different distances in q_x , q_y : (a) 15 nm^{-1} , 15 nm^{-1} and (b) 100 nm^{-1} , 1000 nm^{-1} . The $2\bar{1}\bar{1}0$ Bragg peak is predominantly composed of a central annulus-shaped speckle [367], and can be used to map the orientation and spacing of the $(2\bar{1}\bar{1}0_{WZ})/(20\bar{2}_{ZB})$ lattice planes. By contrast, the diffraction pattern at the $01\bar{1}0$ Bragg peak is made up of many annular speckles scattering over a broad range of q_y originating from the closely spaced stacking fault boundaries illuminated by the beam that act as an interference grating [366]. Any variation in the position or intensity of individual annular speckles within the $01\bar{1}0$ peak encodes differences in the local arrangement and nature of stacking boundaries within the illuminated volume.

By extracting the angle and position of the $2\bar{1}\bar{1}0$ Bragg peak maximum from the coarse nanodiffraction maps (an analysis approach similar to previous work [244, 368, 245]), we find that the lattice orientation varies continuously as a function of position. Figure 4.2(c) shows the twisting of the nanowire about the θ axis (rotation about y_{mot} as defined in Figure 4.1(c)), while Figure 4.2(d) shows the rotation about the incident beam direction (denoted as χ rotation), which is extracted by mapping the $2\bar{1}\bar{1}0$ peak center of mass along q_y . From these maps, we found that the Bragg peak angle varied by $\pm \sim 1.0^\circ$ from the mean in θ , indicating that the nanowire lattice is twisted along its growth axis. Variations of up to $\pm \sim 0.2^\circ$ from the mean in χ also indicate a bending of the nanowire. We note that all nanowires examined showed bending and twisting of a similar magnitude that could arise either during growth or during transfer to the Si membrane substrate. Regardless, the above analysis provides a micron-scale view of the lattice structure that would be useful for monitoring, for example, strain within functioning nanowire devices, and from which one can “zoom in” to specific regions of interest with ptychography.

Further analysis based on the maBPP approach enables reconstruction of a higher-resolution 3D image of strain, and furthermore, provides a means to invert the more complicated speckle patterns measured at the $01\bar{1}0$ Bragg peak into 3D real space images. The reconstructions were performed for the red and cyan regions marked in Figure 4.2(c) for the $2\bar{1}\bar{1}0$ and $01\bar{1}0$ Bragg peaks respectively. Different regions of the nanowire were imaged in order to avoid possible beam induced damage [369], though later measurements reveal the nanowire was structurally robust under continuous focused x-ray probe exposure.

Figure 4.3(a) shows a section of the nanowire (red box in Figure 4.2) reconstructed from the $2\bar{1}\bar{1}0$ Bragg peak nanodiffraction patterns. (Details on maBPP phase retrieval of these data are presented in the Algorithm Description section.) Because this Bragg peak is insensitive to stacking faults in this material, the phase of the reconstruction ($\phi_{2\bar{1}\bar{1}0}$) can be related to the relative displacement of $(2\bar{1}\bar{1}0)$ planes in the direction of the diffraction vector ($u_{2\bar{1}\bar{1}0} = \phi_{2\bar{1}\bar{1}0}/|\mathbf{G}_{2\bar{1}\bar{1}0}|$). 2D cross-sections of the displacement fields are shown in 4.3(b). We note that the reconstruction was performed with the Bragg condition along the white line in Figure 4.3(b) set as a reference. As a result, this region shows relatively flat phase due to the locally homogeneous structure that evolves axially away from the line due to the twist shown in

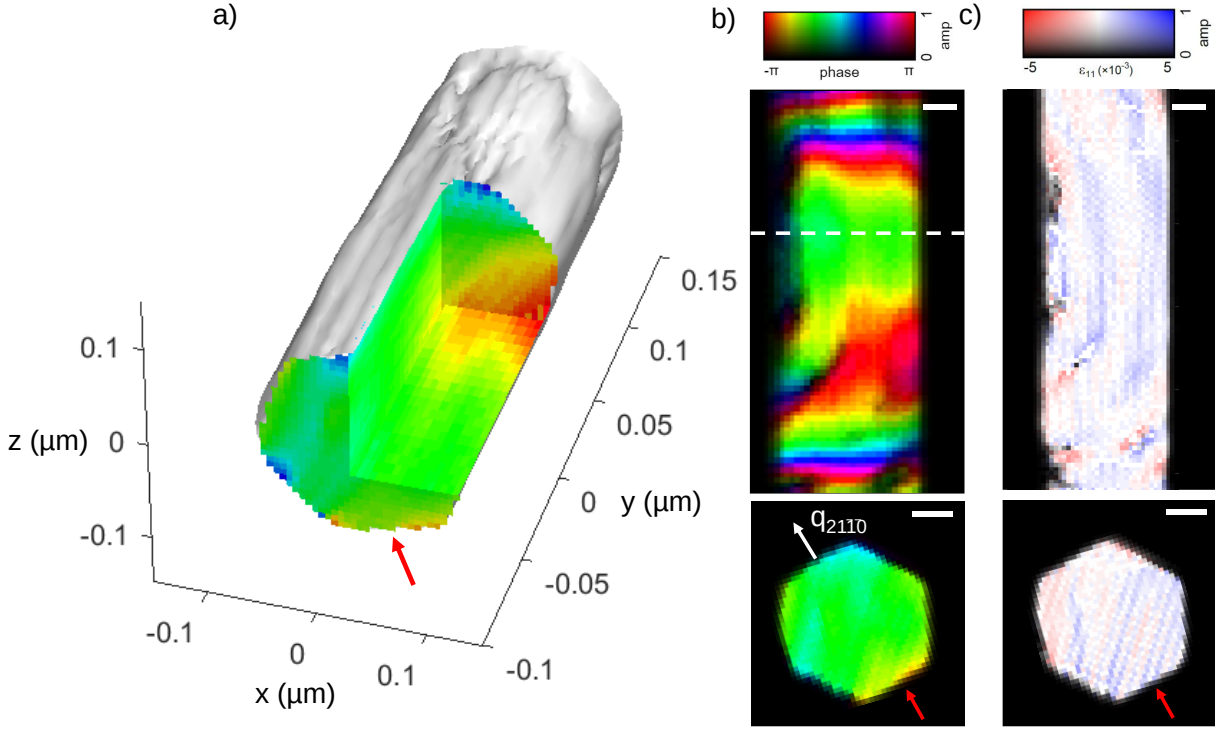


Figure 4.3. maBPP reconstruction of the $2\bar{1}\bar{1}0$ peak. A cut into the 3D reconstruction (a) and 2D cuts (b) taken from this volume. The cross-section cut was taken from the line marked (dashed white). This reconstruction gives sensitivity to lattice displacement along $q_{2\bar{1}\bar{1}0}$ (white arrow). The same 2D cross-sections converted to strain (ϵ_{11}) (c). Pixels at which the strain derivative wraps over in phase are not shown, as they are non-physical. Red arrows identify the nanowire facet that was adhered to the Si substrate. All scale bars are 50 nm.

Figure 4.2. These same cross-sections converted to units of relative compressive/tensile strain along the diffraction vector are shown in 4.3(c), derived via the spatial derivative $\partial u_{2\bar{1}\bar{1}0}/\partial x_{2\bar{1}\bar{1}0}$ [370], where $x_{2\bar{1}\bar{1}0}$ is defined as the direction normal to the $2\bar{1}\bar{1}0$ planes. Further, analysis of the change of phase along the growth direction reveals that outside a length window of ~ 60 nm the lattice orientation varies appreciably ($>10\%$ change) by the twist observed in Figure 4.2. However, we find that this twist does not strongly influence the strain component $\partial u_{2\bar{1}\bar{1}0}/\partial x_{2\bar{1}\bar{1}0}$, as evidenced by the fact that the strain field across the entire 600 nm window in Figure 3(c) varies by less than $\pm 3 \times 10^{-4}$, the $1\text{-}\sigma$ of the Gaussian distribution of strain values in the volume near the dashed line in Figure 4.3(b). We take this value to be the strain sensitivity limit of this particular measurement, and we note that the striations in strain that fall within

this range in Figure 3(c) are artifacts arising from uncertainty in the incident angle of the beam (See Supplemental Figure S1). Further, the breadth of strain variations is comparable to strain variations expected from random alloy fluctuations assuming a binomial distribution of group III elements on group III sites (see supplementary Figure S2). Therefore, we do not expect significant perturbations of the band structure from any long-range strain variations present in these nanowires.

Finally, we note that an isotropic spatial resolution of ~ 50 nm in x , y , and z was estimated for this image, commensurate with the 53 nm full-width-at-half-maximum of the amplitude of the probe. In the x and z directions, this was done by fitting the amplitude of the facet edges to an error function. In the y direction, since no sharp features were present in the field of view, the estimate is based on the angular extent of the diffraction patterns, which does not exceed the annulus given by the beam size.

In the analysis discussed thus far, nanodiffraction mapping and maBPP have been used to map lattice variations and strain across length scales from a few microns to a few tens of nanometers, but shorter range structure variations in the nanowire can be accessed that have a direct impact on electrical properties. Figure 4.4(a) shows the 3D reconstruction of the $01\bar{1}0$ Bragg peak that is sensitive to lattice stacking order and strain in the nanowire. The maBPP image contains closely spaced regions of alternating phase and amplitude separated by planar boundaries normal to the growth direction. This morphology is consistent with TEM observations of stacking faults and phase boundaries in closely related nanowire systems [362]. A 2D cut of the phase and amplitude variations along the growth direction is shown in 4.4(b). The phase color oscillations across stacking fault boundaries (shown as a line cut in Figure 4.4(c)) correspond roughly with the $[-2\pi/3, 0, 2\pi/3]$ phase shifts expected in the $01\bar{1}0$ Bragg peak structure factor [366]. The $01\bar{1}0$ structure factor is sensitive not only to stacking disorder and crystal phase, but also to changes in lattice orientation and strain. Thus, in this nanowire additional variations in phase beyond those associated with stacking disorder are expected due to the substantial twists in lattice orientation.

The structural information in the $01\bar{1}0$ reconstruction includes multiple components, contains very high spatial frequency information, and thus requires careful consideration. As shown in Figure 4.2, a typical $01\bar{1}0$ coherent nanodiffraction pattern scatters to very high q_y . Such broad “barcode” interference patterns from stacking faults in nanowires have been observed previously with unfocused coherent beams,

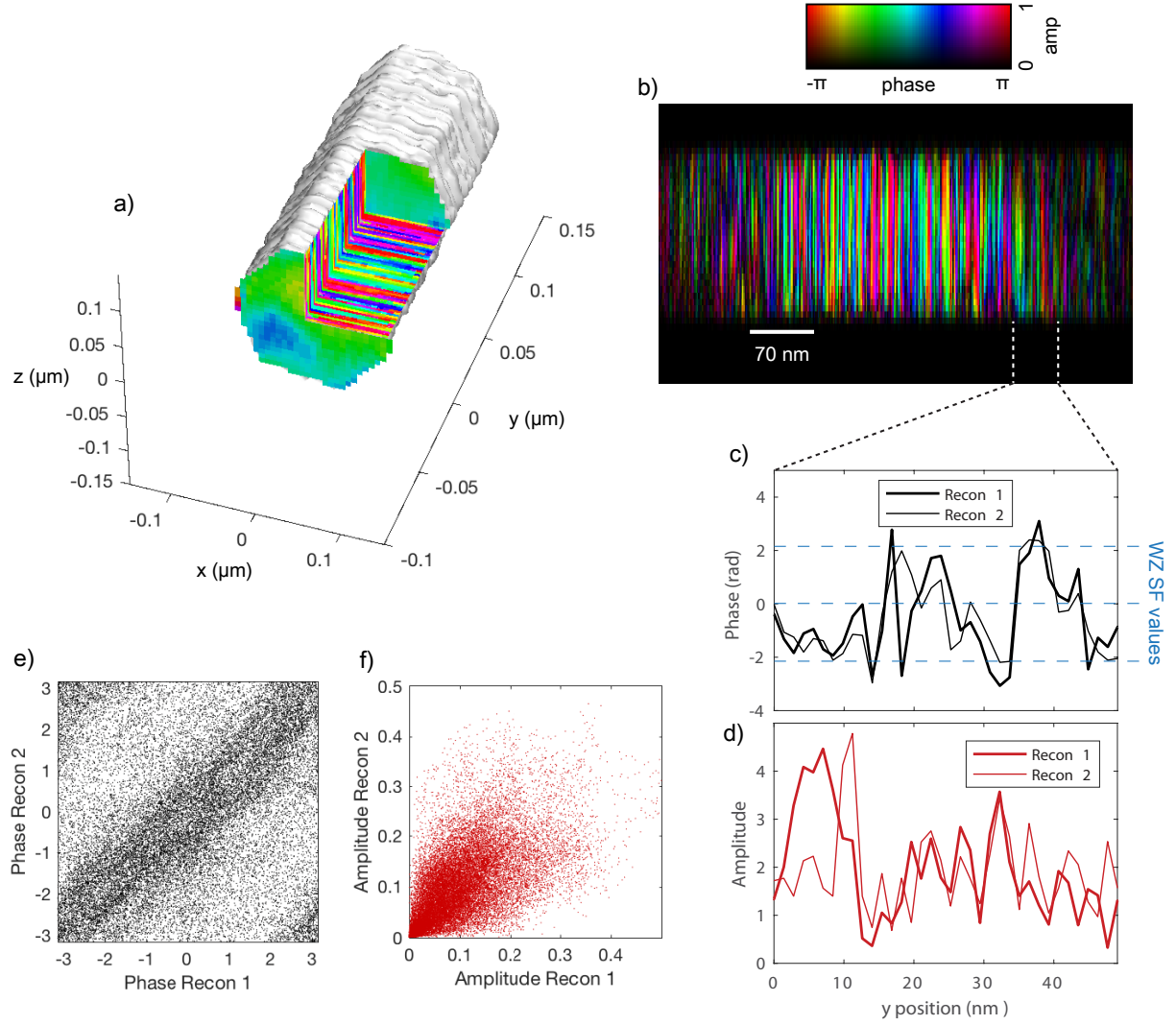


Figure 4.4. maBPP reconstruction of the 0110 peak. A cut into the reconstruction volume (a) and a 2D slice (b) reveal rapidly varying phase features. A line cut of phase (c) and intensity (d) from the center of the nanowire compares two independent reconstructions with different starting guesses to test reproducibility. Correlation tables for every point in the two independent reconstructions show strong phase correlation. Note that the wrapping in phase around 2π results in a concentration of points at the top left and bottom right corners which should fall along the correlation axis (e) The two reconstructions show a lesser degree of amplitude correlation (f). The red arrow identifies the nanowire facet which was adhered to the Si substrate.

and offer the possibility of very high spatial resolution because of scattering to high q_y . In this work, photons were detected to $q_y = 0.48 \text{ \AA}^{-1}$, corresponding to an image pixel size in the y direction of 1.3 nm. (A pixel size of 6.5 nm was used in x and z due to the much more limited extent of scattering observed along q_x and q_z .) However, to date, efforts to invert such diffraction patterns to form an image via standard Bragg coherent diffraction phase retrieval methods have failed due to issues of uniqueness (multiple reconstructions initialized with random numbers yielded different local structures) [348, 366]. Here, we address this issue in two ways. First, we utilize a nano-focused beam such that only a few tens of stacking fault boundaries are illuminated per exposure rather than several thousand, as done in previous studies. Second, we use a ptychography approach that more strictly constrains the solution due to the overlap of the beam positions. Both of these factors help to enable reproducible image reconstructions of stacking faults via maBPP (see Figure 4.4(c-f)).

However, in this particular nanowire, stacking defects can only be reliably characterized over a limited distance along the growth direction ($<50 \text{ nm}$) because of the lattice twist/bend that evolves over the length. Figure 4.2(c) shows that the Bragg peak maximum (θ_{Br}) changes with position. In maBPP, these variations of θ_{Br} from the prescribed reference angle result in additional phase change in the reconstruction. Figure 4.3(b) demonstrates how the long-range twist modifies the phase for a given reconstruction of the $2\bar{1}\bar{1}0$ condition. The $01\bar{1}0$ Bragg peak is sensitive to a different component of the same displacement field shown in 4.3(b). Therefore a phase gradient is present in the resulting reconstruction (Figure 4.4) in addition to the phase variations associated with WZ stacking faults. Thus, interpreting local phases in terms of stacking faults can only be done over length scales for which phase contributions from other structural phenomena are relatively constant (*e.g.* lattice orientation gradients, strain), which is $\sim 55 \text{ nm}$ for the nanowire shown here.

The reconstruction shown in Figure 4.4(b) demonstrates extraction of nanoscale structure in the presence of these additional contributions. The Bragg condition in this reconstruction was set to correspond to the rocking curve maximum in the region of the nanowire near the white dashed vertical lines. The left half of the image therefore contains rapid pixel-to-pixel phase oscillations due to the superposition

of phase contributions from lattice twist, stacking defects, as well as variations due to noise contributions [371], making direct image interpretation difficult. In envisioning an *in-operando* maBPP study on SF characteristics in such a nanowire, more advanced analytical tools are needed that can decouple the components of lattice strain from stacking defects using multiple maBPP images of the same volume, enabling larger fields of view to be interrogated.

Nevertheless, within a 50 nm field of view along the wire axis, as shown, these complicating factors are minimized, and several stacking fault boundaries can be reproducibly imaged. To demonstrate this, phase and amplitude from two different randomly initiated reconstructions (Recon 1,2) are compared for the region denoted in Figure 4.4(b). Line-outs from this region (4.4(c,d)) reproduce well, and a strong correlation is seen for all voxels in the volume bounded by planes parallel to the dotted lines (4.4(e,f)). Within this field of view we can identify ~ 10 WZ stacking fault boundaries that result in $[-2\pi/3, 0, 2\pi/3]$ phase values. The amplitude in this reconstruction is sensitive to ZB phase, but because the ZB inclusions are expected to persist over very small distances (< 1 nm), they will be under-resolved in this image. Given the observation of realistic features expected for these nanowires [362] on the scale as small as 2 pixels, we conservatively estimate an upper bound resolution along the wire axis of 2.6 nm ($2 \times$ pixel size). (Supplemental Figure S3 shows reconstructions from simulations of a lower stacking fault density nanowire in which this spatial resolution estimate is more clearly demonstrated.) We note that many if not most III-As nanowires can be grown with a much lower density of stacking defects than the nanowire imaged here, suggesting that the maBPP methodology can be usefully applied to correlate defect density and electronic properties in many nanowire systems of interest. Finally, as in the $2\bar{1}\bar{1}0$ reconstruction, the average resolution along the x and z directions was found to be ~ 50 nm consistent with the limited angular extent of scattering along q_x and q_z . As is in any ptychography experiments, improvements in resolution can be obtained with improved signal-to-noise ratios of the diffraction signal, especially in regions that extend beyond the beam-limited annulus in reciprocal space.

In conclusion, we demonstrated the ability to image a single InGaAs nanowire on many length scales with sensitivity to multiple nanoscale lattice features. In analyzing and reconstructing diffraction patterns from the $2\bar{1}\bar{1}0$ Bragg peak, we found that the lattice orientation varied along the length of the

wire at micron length scales and that the strain field along the wire cross-section was largely unaffected by this long range lattice rotation. Using diffraction patterns measured from the same wire at the 01 $\bar{1}$ 0 Bragg peak, we could reproducibly reconstruct images of stacking defects. This reconstruction evidenced sharp planar boundaries between different crystal phases of WZ structure, as expected. In both cases, phase retrieval was made possible by a multi-angle Bragg projection ptychography approach that accommodates coherent nanodiffraction patterns measured at arbitrary overlapping positions at multiple angles about a Bragg peak, eliminating the need for scan registration at different angles which is impractical with nanobeams. In combination with coarse scanning nanodiffraction measurements, maBPP allowed for structural investigation of a nanowire over three decades of length spanning from several microns to tens of angstroms. By enabling such a capability, maBPP can contribute significantly to our understanding of nanowires and other nanostructures by correlating structure and properties. This capability will be especially complementary to electron microscopy of nanowires on transparent supports and post-operando atom probe tomography of nanowires embedded in devices, and improvements in maBPP spatial resolution and strain sensitivity can be achieved with further development of the method, for example, by implementing simultaneous probe and sample reconstruction.

4.3. maBPP Algorithm Description

maBPP is predicated on a description of coherent scattering from a nanoscale crystal that equates the far-field diffracted intensity pattern measured with an area detector to a general probe position and measurement angle relative to the Bragg peak. These two degrees of freedom, position and angle, are illustrated in Figure 4.1(b,c). A monochromatic beam illuminating a crystal will satisfy a Bragg condition when the scattering vector $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ coincides with a Bravais lattice point $\mathbf{G}_{\text{HKL}}$ of the illuminated crystal. (Here, $|\mathbf{k}| = 2\pi/\lambda$ where λ is the x-ray wavelength.) Small angular deviations from this condition can be expressed in terms of $\mathbf{Q} = \mathbf{q} - \mathbf{G}$. As described in other work, this vector $\mathbf{Q}$ encodes changes in a coherent diffraction pattern due to angular variations along a Bragg rocking curve [206, 372]. A focused-beam nanodiffraction experiment also allows the incident beam to scan a given region of interest in a crystal by scanning the probe position relative to the sample (in this case, using sample stage

motors x_{mot}, y_{mot}). Thus, a general Bragg ptychography data set for a given field of view comprises of $j = 1 \cdots J$ two-dimensional coherent diffraction intensity patterns I_j measured as a function of different probe positions ($\mathbf{r}_j$) at various angles relative to the Bragg peak (θ_j).

Each of these intensity patterns is the squared modulus of the diffracted wave field at the detector, $I_j = |\psi_j|^2$. The quantity ψ_j can be generally expressed in a maBPP experiment as:

$$(4.1) \quad \psi_j = \mathcal{F} \mathcal{R} \mathcal{Q}_{\theta_j} P_{\mathbf{r}_j} \rho.$$

Here, $P_{\mathbf{r}_j}$ is the 3D wave field of the focused x-ray probe positioned to illuminate the crystal ρ according to the translation of the sample stage motors (x_{mot}, y_{mot}). The term $\mathcal{Q}_{\theta_j} = \exp[i \mathbf{r} \cdot \mathbf{Q}_{\theta_j}]$ (where $i = \sqrt{-1}$) is a 3D real-space complex-valued phase term that encodes spatial frequencies corresponding to angular deviations from θ_{Br} , where θ_{Br} is the angle that satisfies the Bragg condition of the crystal. $\mathcal{R}$ is a 3D→2D projection along the $\mathbf{k}_f$ direction, and $\mathcal{F}$ is a 2D Fourier transformation. This construction of ψ_j leads to a general description of a Bragg ptychography data set in which the probe position and angle are arbitrary and need not be otherwise related so long as the typical degree of probe overlap ($\sim 50\%$) is enforced. In a manner similar to References 242 and 206, Equation 4.1 can be used to derive a gradient that minimizes the sum squared error $\epsilon^2 = \sum_j \| |\psi_j| - \sqrt{I_j} \|^2$ and that can be incorporated into phase retrieval algorithms such as the Ptychographic Iterative Engine (PIE) to reconstruct a 3D image, as was done in this work.

For the maBPP data sets measured at the two Bragg peaks featured in this work, diffraction maps from only strongly scattering angles (indicated in red in Figure 4.2(a) and (b)) were used for image reconstruction. 25 iterations of maBPP with PIE were performed, and a hexagonal-shaped 3D support was used corresponding to the facet orientation of the SEM image in Figure 4.1(a). The diameter of the support for the $2\bar{1}\bar{1}0$ and $01\bar{1}0$ reconstructions was, respectively, 180% and 130% of the nominal wire diameter.

4.4. Limitations and Challenges of maBPP

Despite the success demonstrated in the previous section, maBPP remains challenging experimentally. One obstacle is that resolution in a maBPP reconstruction is limited by the precision with which the

probe and angular positions are recorded. While maBPP does not require positional alignment between angles, the location of the probe positions at each angle must be known with respect to the sample. In this demonstration of maBPP, simultaneous fluorescence mapping was used to align the probe positions between angles using the edges of the nanowire. This corrects for large thermal drifts in the sample that may happen over long scanning times. However, this is only a coarse alignment, which can result in the use of inaccurate probe positions P_{r_j} during phase retrieval. Further, for beamlines that do not allow simultaneous diffraction and fluorescence measurements, the sample position will not be perfectly reproduced between angles, even with minimal thermal drift. Additionally, inaccuracies in measurement of the angular positions of the sample with respect to the incident beam will yield incorrect calculations of $\mathcal{Q}_{\theta_j}$ in the phase retrieval process. For example, for the $2\bar{1}\bar{1}0$ peak in this chapter, only 8 angles were used in the reconstruction (angles shown on rocking curve in Figure 4.2). Reconstructions were attempted with more than 8 angles, but the error in the final reconstruction was higher than that of the reconstruction with 8 angles. This is likely because the additional angles are further away from the Bragg maximum and provide less information, while also being more susceptible to position or angular misalignment. Modifications to the phase retrieval process have been developed that add an extra iterative step to slightly modify, or “anneal”, the probe positions or angle to allow for additional error reduction, but they have not yet been implemented on experimental Bragg ptychography datasets [373, 374, 375]. Measurement inaccuracies can also be reduced during scanning through improvements in beamline hardware.

Despite improvements in algorithms and hardware, there is still a significant hurdle to broader usage of maBPP for strain mapping in nanocrystals: it is very difficult to formulate generalized experimental guidelines for phase retrieval using maBPP. The guidelines for 3D-BP are relatively straightforward: 3D diffraction patterns sampled by twice the Nyquist frequency should be collected at each probe position and the probe should be scanned with 50% overlap. 3D diffraction patterns at a given probe position are generated by combining the 2D diffraction patterns taken across a full rocking curve at a commensurate probe position. In this case the spatial resolution is determined by the extent of oversampled intensity on the detector plane (for $\vec{q}_x$ and $\vec{q}_y$) and the angular extent of the rocking curve (for $\vec{q}_z$) This results in

a highly constrained phase problem, but as discussed previously, it is unrealistically time intensive. For maBPP, the measurement parameters are much more flexible. The number of angles, sparsity of angles, probe overlap, and detector sampling are all convolved, meaning the constraints needed to achieve a desired resolution are not well defined. In fact, it is not even straightforward to specify measurement conditions that will yield a sufficiently constrained phase. Additionally, the amount of material probed in a single projection $\mathcal{R}P_{r_j}\rho$ is dependent on the Bragg condition and sample orientation/geometry, as described in Figure 2.9. Because the information collected at each probe position is not the same for all experiments, the relationship between phase retrieval constraints and experimental conditions is more complex.

In the near future, diffraction-limited storage rings will become more readily available, which offer nano-focused X-ray beams with increased flux and coherency. These probes will allow for faster collection of oversampled intensity patterns, meaning more angles and probe overlap can be collected within a scan series while maintaining reasonable experimental times (a few hours for a maBPP dataset). One might anticipate that a maBPP measurement can record intensity patterns at conditions that far exceed what is needed to constrain the phase problem, i.e. moving towards the limit of collecting full rocking curves like 3D-BP but without the need for precise probe alignment. In the time being, some general empirically derived guidelines can be given based on the maBPP measurements described in this chapter. 2D diffraction patterns should be sampled by twice the Nyquist frequency in the detector frame and the probe should have at least 50% overlap. Rocking curves of high angular density ($>0.02^\circ$) should be collected over the FWHM of the Bragg peak, with intensity patterns at the center of the Bragg peak being most critical.

CHAPTER 5

Correlative Tomography of InGaAs QWs in Nanowires

In this chapter, the techniques discussed in Chapter 2 will be applied in a correlative fashion to investigate the structure and properties of InGaAs QWs embedded in GaAs nanowires. Section 5.1 aims to interpret an observed blue shift in emission within a WZ region of a WZ/ZB axial QW heterostructure. Spatially resolved CL is used in direct correlation with EBSD and nano-probe X-ray diffraction to identify the WZ regions of the QW and rule out strain as the primary contributor to the blue shift. Then CL is directly correlated with 3D atom probe tomography measurements of the nanowires, revealing an increase in the In content within the WZ region of the QW. Measurements of the crystal structure, strain, morphology, and composition are used as inputs to band structure calculations to explain reproduce the measured blue shift in emission. Section 2.4.2 describes InGaAs QWs with an asymmetric thickness profile grown on GaAs cores to study how variations in QW thickness, which frequently occur within nanowire heterostructures, influence nanowire emission. Knowledge of composition, structure, and strain is also required to explain emission characteristics.

To investigate the strain, 3D Bragg coherent diffraction imaging was performed on the asymmetric QW nanowires at two scattering conditions. For the first time, 3D BCDI images probing in-plane strain in nanowires were reconstructed. These reconstructions reveal phase wraps indicative of dislocations at the largest QW facets. This observation suggests that BCDI of asymmetric QWs could be used to obtain experimental measurements of QW critical thickness in nanowires, which to date are poorly understood. Future work will involve EDS-STEM or APT measurements of the same nanowires to directly correlate composition and strain to the emission. Power-dependent PL spectra have been collected for the nanowires measured in BCDI, but more knowledge of the composition and QW thickness are needed for interpretation. Finally, cross-sectional STEM measurements of representative nanowires are needed to confirm the presence and type of dislocations within the QWs. The two investigations discussed in

this chapter provide examples of how 3D correlative tomography can be used to reveal structure-property relationships in complex nanowire heterostructures.

5.1. Emission Shift in Wurtzite/Zincblende InGaAs Quantum Well Heterostructures

Section 5.1 was reprinted with permission from J. Lahmann, **M.O. Hill**, et al. “Correlated Nanoscale Analysis of the Emission from Wurtzite versus Zincblende (In,Ga)As/GaAs Nanowire Core-Shell Quantum Well” *Nano Letters* 19.7, (2019): 4448-4457. Copyright © 2019 American Chemical Society.

5.1.1. Motivation of Research

This study investigates the influence of the crystal phase on the emission characteristics of (In,Ga)As quantum wells (QWs) on GaAs nanowires (NWs). Ternary group-III-arsenide core-shell QWs have shown great promise in nanowire-based emitters/lasers [376, 50, 23, 295] and detectors/solar cells.[377, 378, 379, 380] Notably, (In,Ga)As-based emitters have the potential to operate at the so-called telecommunication band;[381] such a combination of nanoscale emitters with Si waveguides promises to revolutionize the speed and energy efficiency of on-chip information transfer.[382] Recently, key steps towards nanophotonic on-chip integration of such devices on Si were demonstrated.[383, 47, 384] In this context, GaAs nanowires act as a substrate for QWs, with the entire structure acting as a waveguide to confine light.

When GaAs is grown in nanowire form, one can access both the equilibrium zincblende (ZB) and the metastable wurtzite (WZ) crystal phases,[385, 386, 91, 387] and advances in understanding nanowire growth [81, 388] have recently enabled control over the polytype by both metal-organic vapor phase epitaxy [389, 388] and molecular beam epitaxy (MBE).[86] The distinct optical and structural properties of the WZ polytype provide an intriguing opportunity for band gap engineering using polytype junctions.[76] Indeed, studies of binary GaAs nanowires have established that the band gap energies of both polytypes are the same to within 5 meV,[88, 87] whereas the WZ/ZB interface exhibits a type II band offset of about 100 meV.[92, 93, 91, 390] For binary InAs nanowires, a difference between the ZB and WZ band gap energies of about 60 meV has been reported.[391] However, little is known on the influence of the crystal phase on the band structure of important ternary alloys such as (In,Ga)As.[392] Beyond the

influence of crystal phase, engineering the optical properties of nanowire-based QWs requires a detailed understanding of how composition, QW width, and the associated interface strain impact the band structure,[50, 393, 394, 23, 295] necessitating an integrated approach to nanoscale characterization.

Here we employ a unique combination of spatially-resolved measurement techniques, together with calculations in the framework of $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, to provide a correlative structure-property analysis on the level of single nanowires. We grow GaAs nanowire cores with a WZ segment on a ZB base to overgrow circumferential WZ and ZB (In,Ga)As QWs under identical conditions, exploiting the transfer of the core polytype to the shell.[395, 276, 396] Using cathodoluminescence (CL) spectroscopy and electron backscatter diffraction (EBSD), we observe a 75 ± 15 meV blueshift of the QW emission energy in the WZ segment. A combination of atom probe tomography (APT), coherent X-ray nanodiffraction, and theory enables two dominant contributions to the blue-shift to be identified. First, the In content of the WZ QW is lower than that of the ZB QW, while the QW thickness remains unchanged. Second, compressive strain in the QW induces distinct shifts in the valence band energy in the WZ and ZB segments. Our findings can guide future work on nanowire core-shell heterostructures for a range of applications that exploit quantum confinement and polytype phase engineering.

5.1.2. Results and Discussion

GaAs nanowires were grown by MBE using the Ga-assisted vapor-liquid-solid growth mode,[397, 398] and then radially overgrown with shells to form heterostructures.[50] As illustrated in the inset to Fig. 5.1(a) for sample A, a p-doped GaAs core is followed by an (In,Ga)As QW ($\approx 15\%$ In) sandwiched between two nominally undoped (intrinsic) GaAs layers. The QW is capped with an n-doped GaAs outer shell, resulting in a facet-to-facet diameter of about 260 nm. For measurements that require smaller diameter nanowires, sample B was grown with a reduced core and capping layer thickness (without doping), leading to an overall nanowire diameter of about 145 nm. An overview of the as-grown nanowire ensemble A is given by the scanning electron micrograph in Fig 5.1(a); superimposed are two monochromatic CL maps of the QW emission for energies of 1.35 and 1.39 eV, which highlight the presence of segments emitting at different energies (see also discussion and complementary panchromatic CL map in the Supporting

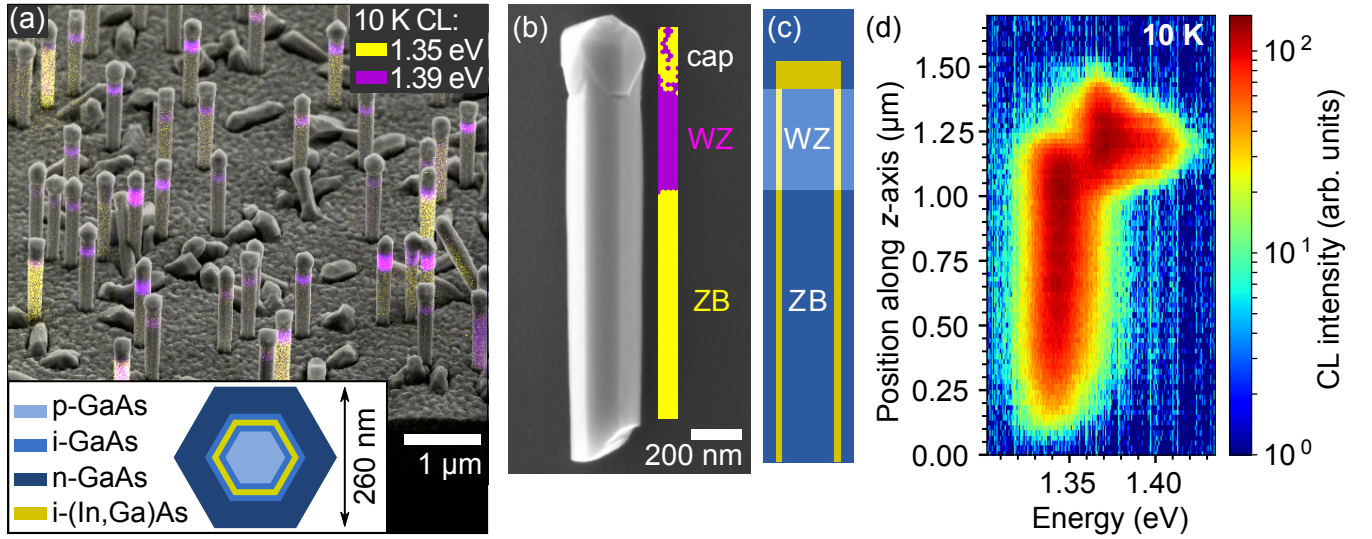


Figure 5.1. (a) Birds-eye view scanning electron micrograph of the (In,Ga)As core-shell nanowire ensemble (sample A). Superimposed are monochromatic CL maps of the low-temperature QW emission at 1.35 and 1.39 eV (false color representation using linear intensity scales). The inset shows a top-view illustration of the core-shell geometry. (b) Micrograph of NW A1 together with a map of the crystal phase recorded by EBSD on the upper facet of this nanowire. (c) Sketch of the axial nanowire cross-section highlighting how the shell QW is grown on the core segments with different crystal structure. (d) CL spectral line-scan along the nanowire axis for the nanowire shown in (b). The emission intensity is color-coded on a logarithmic scale.

Information in reference 399). The origin of this shift in emission energy and its correlation with the crystal structure are investigated in the current study.

5.1.2.1. Correlation of crystal structure and emission properties. . The crystal structure of the nanowire heterostructure was investigated with spatially-resolved EBSD and X-ray nano-diffraction, correlated directly with CL, and independently confirmed by transmission electron microscopy (TEM). Firstly, the variations in crystal structure along the nanowire were determined by EBSD in a SEM for single, dispersed nanowires of sample A, mapping the crystal structure and orientation across the central part of the upward-facing side facet. While the crystal orientation is constant, we consistently observe a transition from ZB to WZ polytype as exhibited by the representative nanowire in Fig. 5.1(b). The base of the nanowire consists of an about 1 μm long ZB segment, followed by about 300–400 nm of the WZ polytype. The cap of the nanowire (≈ 300 nm) exhibits a more complex faceting in the micrograph and an

indeterminate structure due to an insufficient quality of the Kikuchi patterns in the EBSD measurements. Figure 5.1(c) schematically illustrates the structure, where the QW shell (yellow) and capping layer are known to adopt the crystal structure of the nanowire core.[395, 276, 396]

The ZB to WZ transition occurs due to a change in growth conditions. The ZB polytype is grown with a relatively low V/III flux ratio.[82, 91] Towards the end of the core growth, the Ga flux is terminated, leading to the consumption of the Ga droplet. [400, 401] As the droplet shrinks, the contact angle to the nanowire sidewalls is reduced, leading to the nucleation of the WZ polytype.[388, 402] Finally, the cap region results from axial growth during the deposition of the radial shells. The cap is non-emissive and therefore not the focus of the present study.

The crystal structure was spatially correlated with the (In,Ga)As QW light emission from the same nanowire using low-temperature CL spectroscopy. Figure 5.1(d) presents a spectral line-scan along the axis of the nanowire in Fig. 5.1(b). Emission bands are observed at 1.345 and 1.375 eV, and their intensity maxima coincide with the locations of the ZB and WZ segments, respectively. Therefore, the two bands originate from QWs with different crystal structures. A much weaker CL signal around 1.48 eV (not shown), corresponding to the GaAs core, is observed along both the ZB and WZ segments, which confirms the efficient carrier transfer from the core to the QW independent of the crystal polytype. The upper end of the nanowire does not show any significant luminescence, indicating strong non-radiative recombination in this part of the nanowire.

Before discussing the CL results in more detail, we consider a more in-depth analysis of the crystal structure that we obtained from synchrotron-based X-ray nano-diffraction (nanoXRD) measurements. Figures 5.2(a) and (b) show a SEM micrograph and a map of the Ga-K edge X-ray fluorescence (XRF) (taken in conjunction with nanoXRD) for the same representative nanowire from sample A, enabling spatial alignment of the CL and XRD measurements. The integrated diffraction intensity of one of the measured Bragg conditions, $(10\bar{1}0)$, is presented in Fig. 5.2(c). The equivalent to the WZ $(10\bar{1}0)$ reflection is forbidden for the ZB polytype, allowing us to map the position of the WZ segment (about 200–300 nm long) in the nanowire. Figure 5.2(d) shows a map of the CL peak energy, where again a blueshift of the peak emission from 1.345 eV in ZB to 1.380 eV in the WZ segment is obtained.

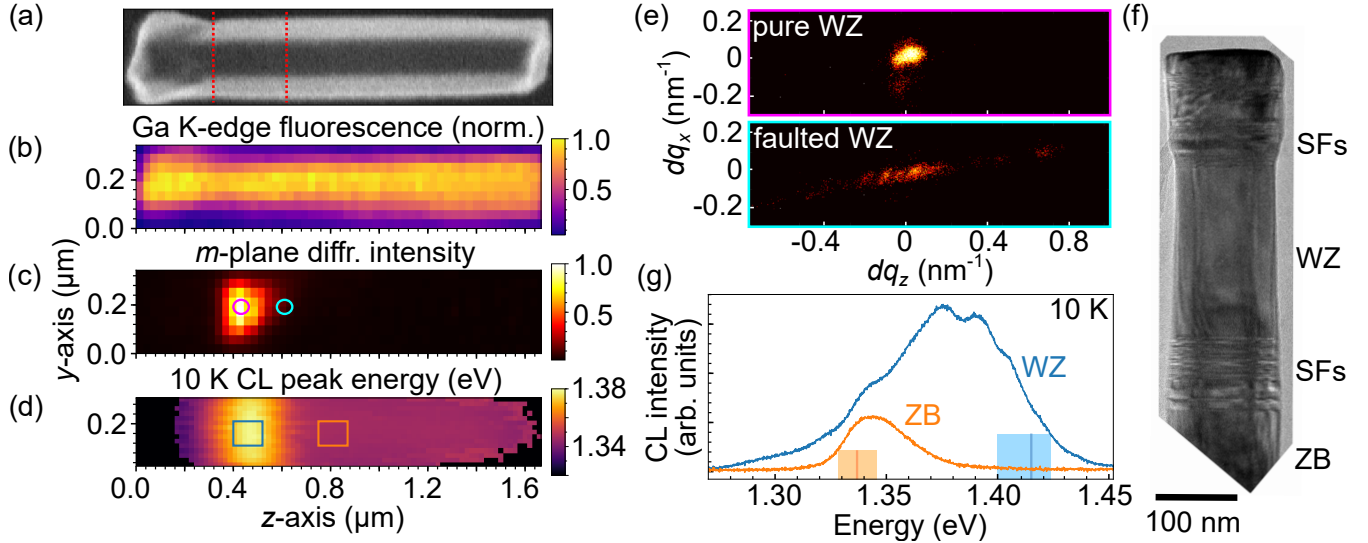


Figure 5.2. (a) SEM micrograph and (b) XRF map of the Ga K-edge for NW A2 used to align the CL and X-ray maps. (c) 2D map of the normalized integrated diffraction intensity for the $(10\bar{1}0)$ reflection (m -plane) forbidden in ZB. (d) Map of the CL peak energy for the same nanowire extracted from a Gaussian fit to the individual spectra of a 2D spectral image. (e) Diffraction patterns for the two positions marked in (c) representing the pure WZ (magenta) and the faulted region (cyan) at the WZ/ZB transition plotted using relative scales. (f) Representative TEM micrograph for a nanowire from sample B (NW B1) optimized for contrast from stacking defects. The presence of the QW is evidenced by its strain contrast. (g) Exemplary CL spectra for the QW emission on the WZ and ZB segments integrated over the regions marked in (d). The markers highlight our estimate of the energy difference between the QW emission from pure WZ and ZB segments.

In addition, nanoXRD is sensitive to the presence of defects in the crystal stacking order of the WZ region. Fig. 5.2(e) shows distinctive diffraction patterns originating from the center of the WZ segment and close to the ZB interface, as marked in Fig. 5.2(c). The diffraction pattern for the center of the WZ region (magenta) appears as a sharp isolated peak indicative of a pure, or nearly pure, WZ crystal. In the transition region close to the ZB interface (cyan), the diffraction spreads to high q_y due to the interference between stacking variations that are smaller than the size of the projected beam.[403, 225, 404] This structure was observed in all eight nanowires measured by nanoXRD. Indeed, a high density of short, alternating segments of WZ and ZB stacking, including stacking faults (SFs) and twins, have been reported for the transition from the ZB to the WZ phase.[398, 402, 82] At the same

time, the central part of the WZ segment appears to be mostly free from SFs, as independently confirmed in Fig. 5.2(f) by TEM for a nanowire of sample B.

Figure 5.2(g) displays CL spectra for the WZ and ZB segment, highlighting that the QW emission from the WZ segment is blueshifted, broadened and can be more intense with respect to the ZB region. From Fig. 5.1(d), we further see that the broadening and blueshift increase from the interface between WZ and ZB to the center of the WZ segment. For the interpretation of the CL measurements, it is important to keep in mind that carriers are excited locally within the scattering volume of the electron beam, but the light is collected from a much larger area. Thus, carriers diffusing to and recombining at a region with lower emission energy will still be attributed to the beam position. Normally, even for QW structures, the III-arsenides have a sufficiently large diffusivity that most carriers excited in the WZ segment should reach the lower energy ZB QW.[405, 406] Nevertheless, we see a clearly blueshifted transition for the WZ QW. Apparently, the stacking defects in the transition region serve as a barrier limiting carrier diffusion to the lower energy segment.

We note that the centroids of the WZ and ZB CL bands are separated by 40 meV, though the sources of broadening and line shapes of these peaks merit a careful consideration (discussed here), and motivate verification via experiment-informed $\mathbf{k} \cdot \mathbf{p}$ calculations (detailed in the next sections). In this material system, the QW emission is inhomogeneously broadened from fluctuations in the composition of the ternary alloy and of the QW width, which introduce carrier localization centers in the QW plane. A significant additional broadening is also present in our data, evidenced by the high energy tail of the ZB band and from the multiplicity of peaks when exciting the WZ segment. The different origins of the broadening in the two polytypes must be considered to infer the blueshift one would expect from pure segments.

Firstly, the peak of the ZB band is shifted towards higher energies due to the high excitation density of the electron beam in CL, which results in the saturation of localized states. The additional contributions probably even include higher excited states in the QW. Therefore, we attribute the low energy slope of this broadened emission band to the QW emission in the ZB segment, as highlighted by the orange marker in Fig. 5.2(g).

Secondly, the strong inhomogeneous broadening in the WZ emission band can be attributed to carriers diffusing to the defective region between the two segments. It has been observed that SFs constitute crystal phase QWs,[91, 101, 387] and when superimposed with a compositional core-shell QW, can act as quantum rings, resulting in an up to 50 meV red-shift of the emission with respect to the compositional QW.[396] Carrier localization at the quantum rings could also explain the increase in emission intensity in the WZ as compared to the ZB segment. The significant broadening of the WZ band is therefore consistent with the red-shift from carriers diffusing to the quantum rings, indicating that the emission of the QW in the pure WZ region produces the higher energy slope, as highlighted by the blue marker in Fig. 5.2(g). Note that, in contrast to ZB, the carrier diffusion to the quantum rings effectively reduces the excitation density in the WZ QW.

Taking these effects into account, we estimate that the WZ QW emission is blueshifted by 75 ± 15 meV with respect to that of the ZB QW. This estimate is based on inferring the energies of the QW emission lines for WZ and ZB that are unbroadened and unshifted in a manner consistent with previously observed phenomena. Importantly, the validity of this analysis can be tested and deeper insights can be attained by invoking further experiments, analyses, and calculations, as presented in the following.

5.1.2.2. Influence of the polytype on the QW growth. The shift in emission energy between the QWs on the WZ and ZB nanowire segments could arise from differences in the band structure of the two polytypes. [407, 408] However, the difference in crystal structure could modify the growth of the QW, resulting in a difference in QW composition, thickness, or strain state, each of which would influence the emission. Here, either thinner QWs or a lower In content on the WZ segments would lead to a blueshift as observed. In order to deconvolve the influence of QW composition and morphology from that of the crystal structure, APT measurements, which provide a three-dimensional, spatially-resolved view of the nanowire heterostructure, were correlated directly with CL.

Sample B, which has a reduced diameter but the same evolution of crystal structure [*cf.* Fig. 5.2(f)], was used for APT, as the large diameter of the nanowires from sample A would require very high voltages for evaporation leading to a high probability of fracture. As APT is destructive, CL measurements were carried out prior to the APT analysis. nanowires were isolated using a tungsten micro-manipulator tip

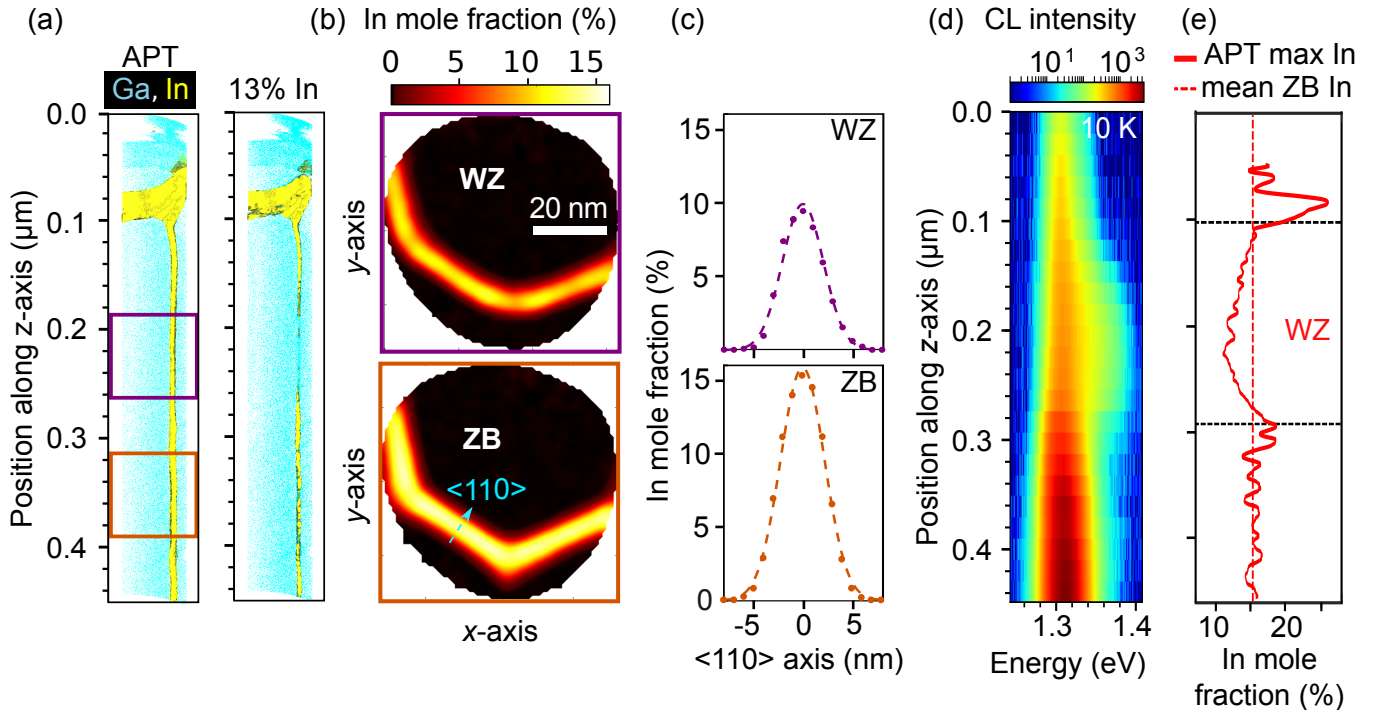


Figure 5.3. (a) APT data for one side facet of a nanowire from sample B (NW B2) represented as two-dimensional cut along the nanowire axis through the APT data on the nanowire side facet with color-coded composition. The map shows 0.5% of Ga atoms in blue, and 100% of In atoms in yellow, while As atoms are omitted for clarity. The outline of the QW is highlighted by the isosurface for a mole fraction of 8%. In the right panel, the isosurface for a mole fraction of 13% In is mapped and filled in yellow. (b) Top-view cross-sections of the In mole fraction extracted from the APT data for the WZ and ZB segments as marked in (a). (c) 2D slices in the center of the QW in the $\langle 110 \rangle$ direction, indicated by the dashed line in (b). Representative line profiles are shown for both WZ and ZB, with Gaussian fits to extract the maximum (dashed curve). (d) CL spectral line-scan recorded along the axis of NW B2. (e) Plot of the maximum In mole fraction, determined along the length of the nanowire by averaging maxima of the QW profiles exemplified in (c). This profile was used to determine the In contents used in emission simulations.

in a dual-beam SEM. In order to align the limited radial field of view of APT with the QW region, the nanowire was intentionally tilted when mounting (see Supporting Information in reference 399), such that mainly one side facet of the nanowire is probed. This specific geometry allowed us to probe the QW along a length of 400–500 nm and thus measure both the WZ and ZB regions in a single wire. A 2D slice in the center of the reconstructed nanowire is shown in Fig. 5.3(a) (for a 3D animation of the APT data,

see Supporting Information in reference 399). At the top of the nanowire, axial GaAs and (In,Ga)As segments are visible, corresponding to the lengthening of the nanowire during growth of the QW and outer shell layers. Below this region, a single facet of the (In,Ga)As QW can be seen. To further outline this QW, the isosurfaces corresponding to a mole fraction of 8% In are highlighted. The right panel in Fig. 5.3(a) shows an isosurface contour for 13% In mole fraction, in which the interior of the contour has been filled in (yellow). The gap in the isosurface indicates that there are compositional variations along the length of the QW. Specifically, the In mole fraction is reduced in the upper part of the probed QW. The purple box coincides with the region of higher emission energy in CL, as shown in Fig. 5.3(d), suggesting it corresponds to the WZ segment of the nanowire.

Cross-sectional views of the WZ and ZB QWs are shown in Fig. 5.3(b). Profiles of the In mole fraction taken along $\langle 110 \rangle$ directions [Fig. 5.3(c)] confirm that the In fraction is lower in the WZ QW. However, the FWHM of the QW, extracted by a fit with a Gaussian, is the same (4.7 ± 0.5 nm) within the experimental error. The variation in QW composition along the length of the nanowire is plotted in Fig. 5.3(e), spatially aligned with the CL map in Fig. 5.3(d). The average In mole fraction in the ZB QW is 15.3% with a symmetric variance of 0.9%, which is comparable to the systematic error in the APT measurement of about 1%. [409, 410] In contrast, the WZ segment exhibits continuous gradients in composition from the interface regions to the center of the segment, and these correlate well with the shifts in emission energy seen in Figs. 5.1(d) and 5.2(d), as well as the inhomogeneous broadening discussed further below. The minimum of the In mole fraction is $10.7 \pm 0.1\%$, where the reported uncertainty is determined by counting statistics and is therefore a lower bound. Assuming that any systematic measurement errors are the same for the WZ and ZB segments, we find a maximum difference in In mole fraction of $4.6 \pm 0.2\%$.

An influence of the underlying polytype on the shell composition and thickness in nanowires has previously been reported for different III-V material combinations such as GaAs/InAs,[411] GaAs/(Al,Ga)As,[329] InAs/InP,[412] and GaAs/ Ga(As,Sb).[413] It is evident that (In,Ga)As/GaAs also exhibits this behavior, as the presence of the WZ segment results in a lower In content as compared to the ZB region.

5.1.2.3. Simulations of the shift in emission energy. In order to calculate the difference in emission energy, we must also consider the possible influence of QW strain. Therefore, nanoXRD measurements

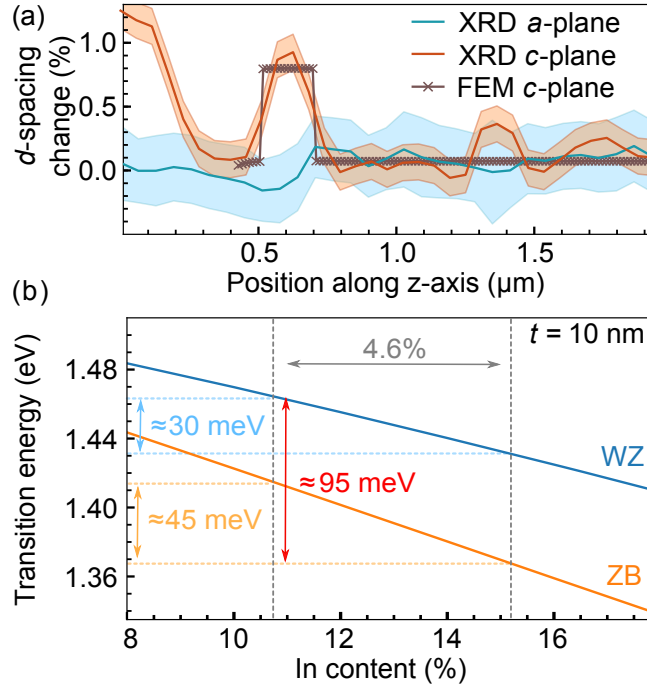


Figure 5.4. (a) Line profiles of the relative d -spacing change (with respect to bulk ZB GaAs) for the a - and c -plane reflections as obtained by nanoXRD on sample A (NW A3) compared with FEM calculations for the c -plane. The experimental error is shown as semi-transparent bands. (b) Transition energies obtained from two-dimensional in-plane $\mathbf{k} \cdot \mathbf{p}$ calculations across (In,Ga)As core-shell heterostructures for varying In content at constant QW thickness t . The dashed lines highlight the change in transition energy expected for a change in In content of 4.6%, amounting to 30–45 meV when ignoring and 95 meV including polytype effects, respectively.

of the relative d -spacing along the nanowire axis [355, 414] were performed on nanowires from sample A [example in Fig. 5.4(a)]. For more details about this analysis see Appendix C. Within the accuracy of the experiment, the a -plane spacing $[(2\bar{1}\bar{1}0)/(20\bar{2})]$ is unchanged along the whole nanowire. In contrast, the c -plane spacing $[(0002)/(111)]$ is increased by $0.9 \pm 0.2\%$ in the WZ segment. Finite element calculations (FEM) based on literature values for the lattice spacing in binary WZ and ZB GaAs nanowires[415] predict a change in c -plane spacing of 0.8%. Hence, we can conclude that the change in c -plane spacing arises primarily from the change in crystal structure, and any residual strain (if present) is below the accuracy limit of our measurement. Further, FEM suggests that changes in the thickness or composition of the (In,Ga)As QW lead to minimal changes of the strain state of the GaAs core (see Supporting

Information in reference 399). Therefore, though the (In,Ga)As QWs are compressively strained from the surrounding GaAs, we conclude that the variation in residual strain between the QWs grown on WZ versus ZB can be neglected.

Now, understanding the composition, morphology, and strain in the QW, as well as the crystal structure of the nanowire, we can simulate the electronic characteristics of the QWs in the WZ and ZB phase via $\mathbf{k} \cdot \mathbf{p}$ calculations. First, we have independently modeled the electronic properties of the ZB and WZ segments based on their equilibrium lattice constants (see Supporting Information in reference 399 for a careful evaluation of the employed material parameters). Second, for both the WZ and ZB polytype, the composition of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ shell QW has been systematically varied and the resulting transition energy, defined as energy difference between electron and hole ground state $E(\Psi_{\text{el}}^0) - E(\Psi_{\text{ho}}^0)$, is shown in Fig. 5.4(b). Because excitonic effects and the role of the excitation density are not taken into account, the absolute transition energies are not expected to be reproduced, but the relative changes should be fairly accurate.

Experimentally, we observe a maximum change in In content between the QW on the WZ and ZB segments of $4.6 \pm 0.2\%$, accompanied by a 75 ± 15 meV shift in the transition energy. According to the calculations, a shift of 30–45 meV could be produced by a 4.6% change in QW composition, depending on whether we take the band parameters for WZ or ZB [marked by dashed lines in Fig. 5.4(b)]. However, the $\mathbf{k} \cdot \mathbf{p}$ calculations also predict that an additional 50–65 meV shift results from the difference in band structure between the ZB and WZ polytypes. This is a significant finding, as an interpolation of the experimentally-observed band gaps in binary alloys would predict a shift of only 10 meV in unstrained $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$. [88, 87, 391] However, for an In content of 15%, the ternary QWs experience a compressive strain of about 1.1% from the lattice mismatch with the GaAs core and outer shell. The opposing impact of this strain on the valence band energies in WZ and ZB (In,Ga)As accounts for the remaining shift in energy. Through the crystal field splitting, the heavy hole valence band dominates in WZ (in contrast to the light hole band in ZB) and is shifted to lower energies; a similar effect has been observed when mechanically introducing strain in binary ZB and WZ GaAs nanowires. [416, 417] In addition, for our QW structures, the different nature of the valence band in WZ also enhances the confinement of the

hole states, introducing an additional increase of the transition energy (see Supporting Information in reference 399 for further details).

The combination of the strain effect on the band structure and the change in In content add up to a predicted blueshift of about 95 meV. The slight overestimation compared with the experiment can be attributed to uncertainties concerning the employed WZ band parameters.

5.1.3. Methods

Growth. The investigated samples were grown by molecular beam epitaxy (MBE) on p-type B-doped Si (111) wafers covered with the native oxide. The MBE system is equipped with one In and two Ga effusion cells, as well as Be and Si effusion cells for dopants and two valved cracker sources for supply of As₂. An optical pyrometer was used to measure the substrate temperature. Fluxes were calibrated and expressed in terms of an equivalent growth rate on the GaAs (001) surface in monolayers per second (ML/s).

Before growth, the Si substrates were annealed in the growth chamber for 10 min at 680 °C. Then, the substrate temperature was adjusted to 645 °C for the growth of the GaAs nanowire core by the self-assisted vapor-liquid-solid (VLS) method. The core growth[418] was initiated by the deposition of Ga for 30 s at a flux of 1.3 ML/s. After a 60 s ripening step without flux, the Ga and As₂ fluxes were supplied simultaneously at a Ga flux of 0.3 ML/s and a V/III flux ratio of 2.2–2.8.[419] The growth time was 30 min., after which the Ga shutter was closed and the VLS Ga droplets on top of the nanowires were consumed by crystallization to GaAs under an As₂ flux of 4 ML/s. Subsequently, the substrate temperature was reduced to 420 °C for the lateral shell growth under a V/III flux ratio of 20, conditions that limit adatom diffusion on the nanowire sidewalls.[50] Two different samples, A and B, with the following multi-shell structure were grown:

Sample A: A full light emitting diode (LED) structure consisting of a radial p-i-n structure. The GaAs nanowire core is doped p-type using Be and has a diameter of about 100 nm. The multi-shell structure consists of (from the core to the outer shell) a 10 nm thick undoped GaAs shell, a 10 nm thick

$\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ QW shell, another 10 nm thick undoped GaAs shell and a 50 nm thick n-type GaAs outer shell doped with Si.

Sample B: To reduce the nanowire diameter for the APT measurements, sample B consists of a 85 nm thick undoped GaAs nanowire core with a multi-shell structure consisting of a 10 nm thick $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ QW shell and a 20 nm thick undoped GaAs outer shell.

It was verified that the difference in doping and diameter between samples B and A did not influence the crystal structure.

Electron backscatter diffraction. EBSD in a SEM allows to determine the crystal polytype of extended segments in GaAs nanowires.[420] To this end, a Zeiss Ultra 55 field-emission SEM equipped with an EDAX/TSL EBSD system was operated at an acceleration voltage of 20 kV and a beam current of 1.7 nA. nanowires were dispersed on a Si substrate covered with Au-markers to facilitate subsequent CL measurements on the same nanowire. The sample was tilted at 70° and the axis of the probed nanowire was aligned along the vertical direction. EBSD maps were acquired with a step size of 20 nm, though the interaction volume of the backscattered electrons and thus the actual spatial resolution is estimated at about 50 nm. The recorded Kikuchi patterns were automatically indexed using the provided routines of the manufacturer. Note that each of the correlations presented in the manuscript was verified on several nanowires to ensure that the conclusions we draw can be generalized.

Cathodoluminescence spectroscopy. CL spectroscopy was carried out in the same SEM, which is also equipped with a Gatan monoCL4 system, at an acceleration voltage of 5 kV and beam currents of about 500 pA. A diffraction grating with 600 lines/mm blazed at 800 nm was used in conjunction with a slit width of 0.5 mm (hyperspectral maps) and 2 mm (monochromatic maps), which corresponds to spectral resolutions of about 4 and 16 meV, respectively. The luminescence was detected by a photomultiplier tube (PMT) for monochromatic maps and by a charge-coupled device (CCD) for hyperspectral maps. Hyperspectral line-scans along the axis of single nanowires were collected by recording the luminescence spectra using the CCD at each dwell point of the electron beam. Note that the PMT is close to the limit of its detection range for the probed QW emission and its sensitivity is not corrected for, whereby shifts in the emission energy from nanowire to nanowire and between the WZ and ZB segments can have

a significant impact on the recorded intensity in Fig. 5.1(a). The samples were cooled to 10 K using liquid He with a dedicated stage. The correlation to EBSD and nanoXRD was carried out on dispersed nanowires from sample A. Prior to the APT measurements, as-grown nanowires close to the cleaving edge of sample B were measured with the sample mounted at an angle of 90° . The positions were documented by overview micrographs to facilitate harvesting of these very nanowires. CL data analysis was performed using routines based on the python library hyperspy.[421]

Nanoprobe X-ray diffraction. Nano-diffraction measurements were performed at the Hard X-ray Nanoprobe beamline 26-ID-C of the Advanced Photon Source at Argonne National Laboratory. Simultaneous X-ray fluorescence mapping of the Ga K-edge (10.367 keV) was used to locate the nanowires, which were randomly dispersed on a 10 μm thick Si substrate transparent to hard X-rays. A nanofocused beam of ≈ 25 nm diameter was scanned across the nanowires, and diffraction patterns for a specific Bragg reflection were measured on a 2D CCD detector placed 0.8–0.9 m away from the sample. A total of eight nanowires were measured at 2–3 different Bragg conditions each. nanowires oriented in two different directions on the substrate were measured, which gave access to different Bragg reflections. The first set of nanowires, which includes NW A2 from Fig. 5.2, were investigated at the *a*-plane condition of $(2\bar{1}\bar{1}0)$ and the *m*-plane $(10\bar{1}0)$ reflection (forbidden for ZB). The second set of nanowires, including NW A3 from Fig. 5.4(a), was investigated at the same $(2\bar{1}\bar{1}0)$ reflection, but also at the *c*-plane condition of (0002) and the $(10\bar{1}1)$ reflection, which has components of both *c* and *m*-planes (forbidden for ZB). Whereas the first set of nanowires did not allow access to the *c*-plane reflection, they gave a better view of the stacking order using the *m*-plane reflection.

Atom probe tomography. Samples for APT were prepared by a multi-step transfer method in a SEM (see Supporting Information in reference 399 for images).[422] First, a sacrificial nanowire was Pt welded to the end of a tungsten micromanipulator tip. The sacrificial nanowire was then welded to the base of the nanowire of interest that was standing vertically (as grown) on the edge of a Si substrate. The nanowire was then pulled off the substrate, the SEM was vented, and the manipulator tip was rotated by hand to tilt the vertically standing nanowire by approximately 30° . The nanowire was then Pt welded to the top of a tungsten tip standing vertically in the SEM and the sacrificial nanowire was broken off. The

nanowires were then cleaned in oxygen plasma for 3 min. The nanowire diameter of 145 nm (short axis) is still significantly larger than common for APT tips. In this case, mounting to tungsten tips was essential for the analysis of the nanowire without fracture, which was not possible using a traditional Si micropost array. APT measurements were performed in a LEAP 5000XS system utilizing a 355 nm laser, at a 30 K stage temperature, 250 kHz laser pulse rate, and a 2% detection rate. A pulse energy of 10 pJ was used to evaporate through the overgrowth layers, and then was lowered to 1 pJ, with the specimen reaching a maximum of 2.5 kV. The APT measurements are consistent for a total of three analyzed nanowires.

Simulations. Calculations based on $\mathbf{k} \cdot \mathbf{p}$ perturbation theory are well adapted to assess the properties of multiple conduction and valence bands around the center of the Brillouin zone with a reasonable computational effort.[423] Elastic and electronic properties were computed using the respective modules of the Sphinx software library.[424] In this framework, we employ an eight-band $\mathbf{k} \cdot \mathbf{p}$ model for WZ semiconductor materials.[425] As the segments are long enough that we can ignore the influence of the interfaces on their elastic properties, the calculations have been restricted to 2D in-plane cuts through the nanowire [c.f. sketch in the inset to Fig. 5.1(a)]. The calculated structure corresponds to that of sample B. The parameters of the ZB phase were transformed to the ones of the WZ Hamiltonian using the relations provided in Ref. 426. All relevant parameters employed are summarized in the Supporting Information in reference 399 (using the WZ notations) together with a discussion on their reliability. Elastic strain was computed using a linear elasticity model and enters the eight-band $\mathbf{k} \cdot \mathbf{p}$ model in a similar manner as in Ref. 408. Excitonic effects were neglected in this work and thus represent a systematic error (of about 5–10 meV[427]) to be considered when comparing simulation results to transition energies observed in experiment.

Transmission Electron Microscopy. nanowires from sample B were investigated by high-resolution TEM in a JEOL 2100F field emission microscope operated at 200 kV and equipped with a Gatan Ultra Scan 4000 CCD camera for image recording. For this investigation, the nanowires were mechanically dispersed on a Lacey carbon film supported by a 300 mesh copper grid. Each investigated nanowire was aligned along the $\langle 11\bar{2}0 \rangle$ WZ zone axis (corresponding to the $\langle 1\bar{1}0 \rangle$ ZB zone axis) to obtain high resolution micrographs and a clear contrast from SFs.

5.1.4. Summary and Conclusions

In summary, the concurrent growth of (In,Ga)As QWs on adjacent ZB and WZ templates in the form of GaAs nanowire cores, together with a suite of spatially-correlated single nanowire measurements, allowed us to establish the influence of the crystal polytype on the growth and emission properties of these ternary QWs. For the WZ QW, we find a reduced In mole fraction and an enhanced influence of strain on the band structure through a shift in the valence band. Both of these factors contribute to the observed blueshift in emission energy. The influence of carrier localization at the stacking defects in the ZB/WZ interface boundary region, as well as spatial variations in In mole fraction explain the inhomogeneous broadening of the WZ QW emission peak. In consequence, the peak centroid shift of about 40 meV underestimates the difference between the QW transition energies in WZ and ZB, which we estimate to amount to 75 ± 15 meV. Note that this correlative approach can be applied to a variety of open questions concerning the properties of semiconductor nanostructures.

Previously, the emission behavior between WZ and ZB binary GaAs has been studied in detail. However, in nanowire optoelectronic applications, core-shell heterostructures with ternary QWs are much more relevant. Our correlative analysis deconvolves the effects of composition and strain in ternary (In,Ga)As QWs, showing that the difference in emission energy between the WZ and ZB QW regions is much larger than for binary GaAs as a consequence of the compressive strain on the QW. We thereby establish key design principles for the application of crystal properties in engineering III-As emitters.

5.2. Bragg Coherent Diffraction Imaging of InGaAs Quantum Wells of Asymmetric Thickness

As discussed in Chapter 2, correlative imaging is critical for understanding the emission properties of InGaAs QW nanowires. In Section 5.1, atom probe tomography, spatially resolved CL, EBSD, and X-ray nanodiffraction were combined to uncover the origin of a blue shift in CL emission. In that case, 2D nano-diffraction mapping was sufficient to confirm the strain state because the primary variation in strain and structure was along the length of the nanowires. In this section, nanowire InGaAs QWs with different thicknesses on each facet (referred to here as asymmetric QWs) were investigated, requiring 3D imaging of the strain state at high resolution. To this end, coherent diffraction imaging was performed on single nanowires to investigate strain. Strain states within QWs as thin as 4 nm were resolved, and phase wraps within the nanowire cross-section suggest the presence of misfit dislocations at the corners of the largest facets. This work outlines a new approach to coherent diffraction imaging of long nanowire heterostructures, without potentially defect-forming milling or etching processes. Additionally, this section proposes a new method to investigating critical thicknesses for defect formation in multi-shell nanowire heterostructures. The nanowire growth, fabrication, and PL measurements in this work were performed by Paul Schmiedeke in the group of Professor Gregor Koblmüller at TU Munich.

5.2.1. Motivation of Research

Growth of shells on nanowire cores commonly produces non-uniform thickness on each facet [428]. Furthermore, nanowires cores can exhibit deviations from a perfect hexagon; the shells grown on these cores will adopt the same shape [429]. Until recently, simulations of electronic behavior have been limited to perfect hexagons with uniform QW thicknesses throughout. A wavefunction delocalization with six-fold symmetry (with greatest amplitude at each QW corner) is predicted. However, recently, Sonner et al. [430], calculated that $<2\%$ thickness variations between facets of AlGaAs QWs on GaAs will lead to a redistribution of carriers. They calculated that for a 5.5 nm QW heterostructure with a single wider QW facet, if the wider facet is 5.6 nm (0.1 nm larger), the exciton distribution will localize on the two corners around the 5.6 nm facet. Further, if the wider facet is 6.4 nm (16% larger) the exciton distribution will

be fully localized on the single facet. They hypothesized that such variations in well thickness could lead to emission line broadening and emission center variations in PL.

Calculations to determine the effect of QW thickness variations on emission, like those performed in Sonner et al. [430], require input of QW width, composition, and strain on each facet. In Sonner et al., the low misfit strain of 0.038% in the $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ heterostructures was insufficient to generate dislocations, and the strain fields could be accurately determined by FEM. In contrast, the $\text{InGaAs}/\text{GaAs}$ heterostructures considered here have large misfit strains potentially sufficient to nucleate dislocations in the thicker QWs. In this context, FEM predictions of strain are not sufficient. Therefore three-dimensional probing of strain, composition, and QW morphology are required to support modeling of the carrier distribution, with the goal of determining how carrier localization modifies the PL emission, as was done previously for AlGaAs quantum structures [430]. This section describes investigations of the 3D strain distribution in asymmetric InGaAs QWs grown on GaAs nanowires through Bragg coherent diffraction imaging (BCDI). Directly correlated power-dependent PL measurements were performed by collaborators and will be reported elsewhere. Further work is proposed to measure the composition and QW thickness in the same nanowires via APT or STEM.

5.2.2. Results and Discussion

5.2.2.1. Nanowire growth and processing. GaAs nanowires were grown via a self-catalyzed VLS process in MBE. Selective area epitaxy was used to create an hexagonal array with a 10 μm pitch. SEM confirmed the length and thickness of the nanowire cores at these growth conditions to be $\sim 4 \mu\text{m}$ and $\sim 50\text{-}100 \text{ nm}$ (facet to facet) respectively. Given the Ga flux during growth, the crystal structure is expected to be primarily ZB. After core growth, the substrate was rotated to align the $\{01\bar{1}\}$ nanowire facets with the MBE effusion cells (by aligning to the Si wafer flat). The rotation angle and growth conditions were chosen to grow an InGaAs QW of 4 nm thickness on the closest $\{01\bar{1}\}$ facet. During this directional deposition, QWs on the two adjacent facets are expected to grow at half the rate (to a 2 nm thickness). Next, the substrate was rotated 180° and InGaAs QWs were grown on the other three facets with nominal thicknesses of 10 nm, 10 nm, and 20 nm. Finally, a GaAs barrier layer of $\sim 50 \text{ nm}$

was grown. The expected final structure is shown in 5.5(a), consisting of QWs with nominal thicknesses of 20 nm, 10 nm, 10 nm, 2 nm, 2 nm, and 4 nm on adjacent facets. The final diameter is predicted to be between 200-250 nm (facet to facet) and the In content is nominally $\sim 20\%$. The 2 nm QW serves as a barrier between the 4 nm QW and the 10 and 20 nm QWs to enable PL from the 4 nm and 20 nm wells to be distinguished in power-dependent PL measurements; the larger QWs should dominate emission at low powers, while high power excitation is sufficient to populate excited states including the delocalized states associated with the 2 nm QW. Deviations in the predicted PL emission wavelengths and evolution could be due to variations in composition, QW thickness, structure, or strain. Strain was first investigated using non-destructive BCDI, followed by power-dependent PL on the same nanowires, which will not be reported here. Additional measurements of composition and well thickness are found to be necessary to fully explain the PL.

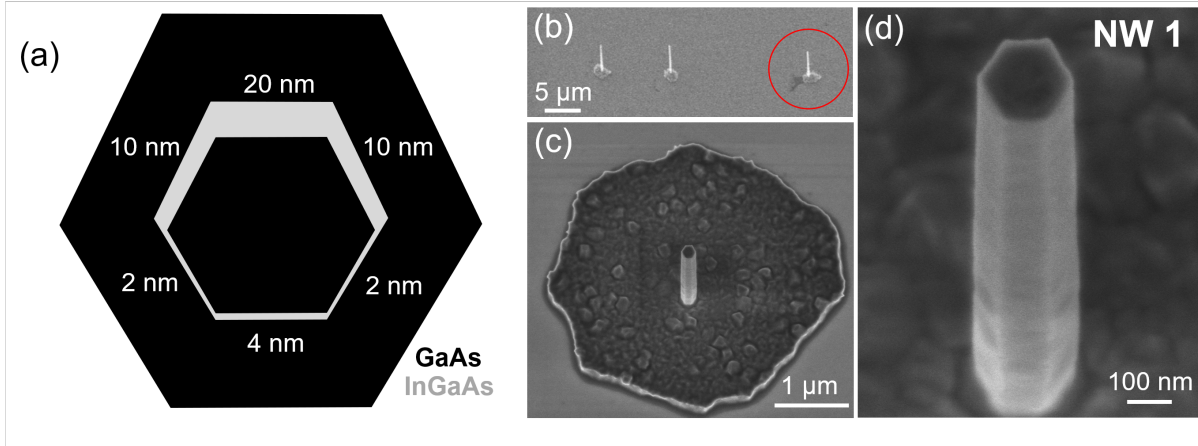


Figure 5.5. Growth schematic and SEM of asymmetric InGaAs QW nanowires (a) Nominal dimensions for asymmetric InGaAs QW grown on GaAs core. Nominal In content is 20%. (b) SEM of three widely spaced nanowires with parasitic growth layer etched away. (c) SEM of NW-1 circled in (b) after shortening. An island of parasitic growth remains around the nanowire. (c) Close up SEM of NW-1, after etching the nanowire length is 1.9 μm and diameter is 206 nm. SEM taken at a 20° angle.

BCDI was used to image the strain in the buried QWs. As described in Section 2.4.2, BCDI requires nanostructures to be fully isolated from materials that diffract into the same region of reciprocal space. To avoid overlapping diffraction patterns, the nanowires were grown in lines separated by at least 10 μm with

the same minimum spacing between wires in a single line, as seen for three nanowires in Figure 5.5(b). Typically, for diffraction of nanowires at in-plane conditions (to probe the strain in the cross-section), nanowires are removed from their growth substrate and redeposited lying down on X-ray transparent substrates, such as described in Appendix A. However, previous studies have shown that the in-plane scattering is highly sensitive to twisting and bending induced at the interface of the lying-down nanowire and substrate [403]. The effects of this bending are shown for the $(01\bar{1})$ condition in Figure 4.2(c)-(e) in Chapter 4, where ptychography was used to reconstruct the nanowire despite the large twisting/bending. BCDI is less able to accommodate spatial variations in diffraction angle (as compared to ptychography), so the nanowires were left in their as grown vertical geometry to avoid substrate induced twisting. Diffraction from single nanowires in this geometry creates other challenges, one of which is diffraction from parasitic growth on the regions between nanowires. At the low temperatures needed to grow high In content InGaAs QWs (420°C) in MBE, a parasitic polycrystalline layer will grow on the SiO_2 . Under the growth conditions used here, a polycrystalline parasitic layer of $\sim 250\text{ nm}$ GaAs and $\sim 40\text{ nm}$ InGaAs forms across the entire substrate surface. If this layer is not removed, it would produce a sparse powder diffraction ring due to the dispersity in orientations of the polycrystals. The vertical nanowire will diffract at a single angle onto this same diffraction ring, producing undesirable overlap that could compromise the reconstruction. To remove the parasitic layer, the substrate was spin-coated with a maP-1240 photoresist, thick enough to fully cover the nanowires, and electron-beam (e-beam) lithography was used to expose the resist around ~ 30 nanowires. The resist was dissolved using acetone and isopropanol, leaving behind the cross-linked regions protecting each nanowire. The parasitic layer was removed with a wet etch of citric acid and hydrogen peroxide, and then the residual resist was dissolved from the nanowires [431]. The results of this process are seen in Figure 5.5(b), where small islands of parasitic material were left at the base of each nanowire (due to limits in alignment during e-beam lithography). In 5.5(c), a close up of the nanowire circled in red is shown, denoted as NW-1. In this case a $4\text{ }\mu\text{m}$ wide island of parasitic growth remained for NW-1; this island did not notably interfere with the nanowire diffraction during BCDI measurements. Other nanowires showed even smaller parasitic layer islands $<1\text{ }\mu\text{m}$ in diameter.

Another consideration when preparing nanowires for X-ray measurements is that BCDI collects the diffraction from the entire nanowire simultaneously. At the end of the core growth, the Ga droplet is consumed by closing the Ga effusion cell, which leaves behind a region of low crystal quality. Diffraction from this region can interfere with the primary nanowire diffraction, preventing reconstruction of the nanowire, so the upper regions were removed prior to BCDI measurements. The substrate was spin-coated again with a S1818 resist to a thickness of $\sim 1.5 \mu\text{m}$, and the nanowire portion above the resist layer was selectively etched away using HCl (to remove the surface oxide) followed by a citric acid and hydrogen peroxide mixture. Since BCDI requires that nanocrystals fit fully within the coherent X-ray beam (typically $1\text{-}2 \mu\text{m}$), the resist layer was deposited such that the remaining nanowire segment was $\sim 1.5 \mu\text{m}$ in length. Figure 5.5(b) shows three of the nanowires prior to shortening. The nanowire circled in red (NW-1) is shown after shortening in 5.5(c),(d). The final nanowire length was $1.9 \mu\text{m}$ and the nanowire diameter was 206 nm , within the range of the predicted diameter.

5.2.2.2. Coherent diffraction imaging measurements. Measuring the strain state of the nanowire QWs requires selection of a diffraction condition sufficiently sensitive to strain in the nanowire cross-section. Until now, to the best of our knowledge, reports of 3D strain reconstruction in nanowires via BCDI has been limited to out-of-plane strain, i.e. mapping the spacing between planes along the nanowire growth direction [217, 218, 219, 220, 221, 222, 223, 224]. For the cases in which in-plane scattering peaks were measured, reconstruction of the real space 3D strain field was not possible [225, 220, 226, 227, 228, 229, 230]. An out-of-plane condition, such as (111) in ZB, is usually chosen because it is a symmetric scattering condition ($\theta = 2\theta$) and is easily accessible for nanowires in the vertical geometry. While out-of-plane strain measurements can probe interesting variations along the nanowire length, they are not ideal for investigating radial nanowire heterostructures with complex variations in in-plane strain. Figure 5.6(a) shows a reciprocal space map with a few relevant scattering conditions for $\langle 111 \rangle$ oriented ZB nanowires (the thickest QW facet is identified with an arrow). The (111) scattering condition that is only sensitive to out-of-plane strain is shown in red. For ZB nanowires, the $\{2\bar{2}0\}$ scattering (blue peak in 5.6(a)) could in principle be used to measure the in-plane lattice spacing, but scattering from this peak is blocked by the substrate. Thus the $\{11\bar{1}\}$ scattering condition was chosen for in-plane strain

imaging. This asymmetric scattering condition has a primary component ($\sim 78\%$) in the horizontal plane (like the $\{2\bar{2}0\}$) with a slight out-of-plane component ($\sim 22\%$). Two of the six $\{11\bar{1}\}$ peaks are shown in black in 5.6(a). The three $\langle 11\bar{1} \rangle$ directions that have vertical components in the $[111]$ direction are shown in 5.6(b) with respect to the asymmetric QW structure (the other three $\{11\bar{1}\}$ peaks have vertical components pointing towards the $[\bar{1}\bar{1}\bar{1}]$ direction, so the diffraction will be into the substrate).

BCDI measurements were performed at the 34-ID-C beamline of the Advanced Photon Source; an example scattering geometry is shown in Figure 5.6(c). A zone plate diffractive optic illuminated the vertical nanowire on the growth substrate, and the 9 keV X-ray beam incident along $\vec{k}_i$ was scattered from the nanowire along the final direction $\vec{k}_f$ onto a charge coupled device detector (CCD). An example 2D diffraction pattern for the $(11\bar{1})$ scattering of NW-1 is shown on the detector. The full 3D $(11\bar{1})$ diffraction peak in reciprocal space is shown in blue, probing the lattice displacement of the nanowire along the momentum vector direction $\vec{q}_{11\bar{1}}$. Vertical and horizontal slits were tuned to maximize the probe size; while a 2 μm vertical probe was desired to illuminate the entire nanowire, the coherency and flux must be maintained, which limited the vertical beam width to 1.05 μm and horizontal beam width to 0.5 μm . It is noted that the vertical width is the limiting factor for fully illuminating the nanowires for BCDI measurements because the nanowires are longer than they are wide. An ASI Quad (512 $\times$ 512) Timpix detector with 55 $\times$ 55 μm^2 pixels was placed at 7.3 $^\circ$ (γ) vertically and 22.9 $^\circ$ (δ) horizontally at a distance of 1 m from the sample. 3D diffraction patterns were collected for 6 nanowires at the $(11\bar{1})$ reflection, and the $(\bar{1}\bar{1}1)$ peak was collected for five of the same nanowires. Figure 5.7(a) shows the relationship between the directions probed and the asymmetric QW structure. Diffraction patterns were collected with a 20 second exposure at angular steps of 0.01 $^\circ$ and an angular range between 1.5-2 $^\circ$ to collect the majority of the 3D reciprocal space patterns.

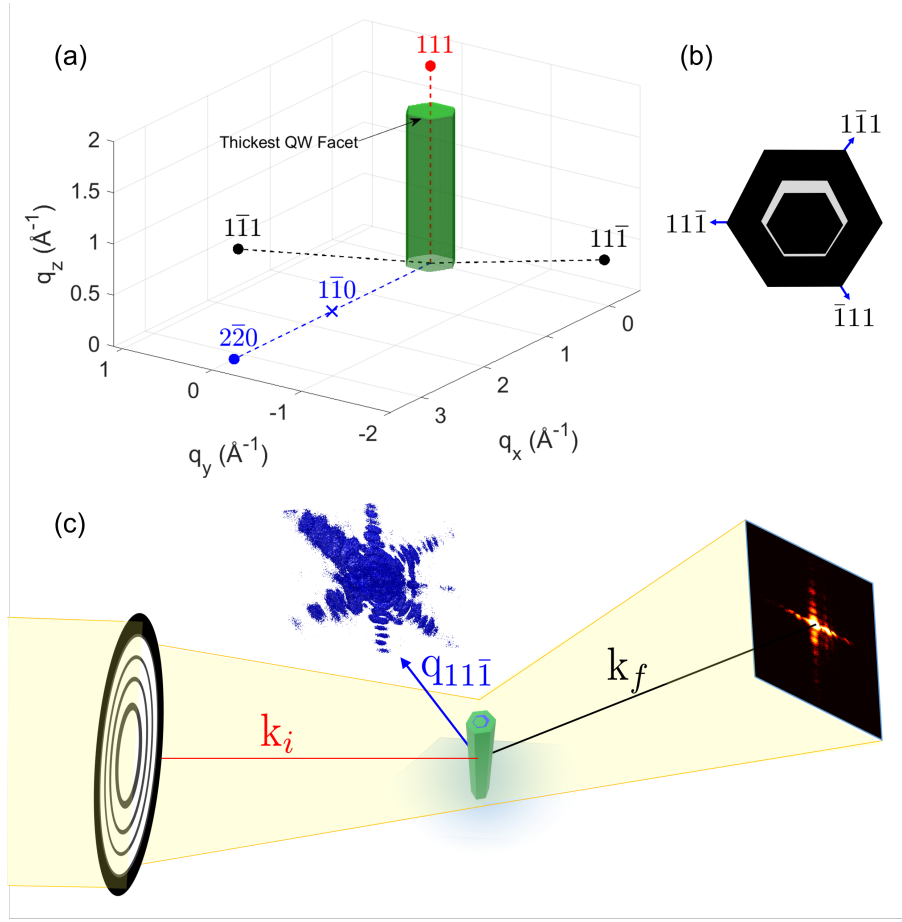


Figure 5.6. (a) A reciprocal space map aligned with the real space nanowire showing available diffraction conditions for BCDI measurements. The (111) condition probes out-of-plane strain; $(2\bar{2}0)$ probes in-plane strain but is blocked by the substrate in this geometry. Asymmetric $\{1\bar{1}\bar{1}\}$ scattering conditions have a mostly in-plane strain component, with a slightly out-of-plane component. (b) View of the in-plane component of the $\{1\bar{1}\bar{1}\}$ peaks with respect to the asymmetric QW facets, $(1\bar{1}\bar{1})$ and $(11\bar{1})$ are investigated in this work. (c) Schematic of BCDI experiment at the $(11\bar{1})$ condition. A zone plate is used to focus the coherent X-rays onto the nanowire along $\vec{k}_i$ diffracting along $\vec{k}_f$ onto a 2D CCD detector. The q -vector points to the location of the reciprocal space peak. The 3D diffraction pattern for NW-1 is shown at this RS point.

5.2.2.3. Interpretation of diffraction patterns and phase retrieval. Figures 5.7(a),(b) show 3D reciprocal space maps (RSMs), a 2D Z-Y cut at the maximum intensity, and a 2D Z-Y cut at the maximum intensity for $(11\bar{1})$ and $(1\bar{1}\bar{1})$ peaks of NW-1. Both 3D RSMs are plotted as isosurfaces of 3 counts. The 8 fringes (6 in a star pattern and in each direction along $\vec{q}_y$) seen for $(11\bar{1})$ in 5.7(a) are

features of the crystal truncation rods from the 6 nanowire side facets and two nanowire end facets. Already an asymmetry in the 6-fold fringes of the diffraction peak can be seen, which is expected for an asymmetric strain field from QWs of variable thickness. It is evident from both the RSMs and 2D diffraction patterns that the signal in the fringes is much stronger for $(11\bar{1})$ than $(\bar{1}\bar{1}1)$. Let us now consider by eye whether 3D BCDI reconstructions are possible for these diffraction patterns. The 6-fold pattern seen on the right for 5.7(a),(b) has a fringe spacing defined by the nanowire diameter. For the $(11\bar{1})$ and $(\bar{1}\bar{1}1)$ peaks respectively, approximately 10 and 8 pixels per fringe period are resolved. For phase retrieval, BCDI requires a sampling of at least twice the highest frequency (Nyquist Frequency) [432, 205]. In other words, at least 2 pixels per fringe must be sampled in the detector. Therefore, the 8 and 10 pixel resolution should be sufficient for reconstruction of the nanowires in the radial cross-section (two of the nanowire dimensions). In the third dimension, the fringe spacing along the nanowire long axis, parallel to $\vec{q}_y$, must also meet the oversampling requirement. Along $\vec{q}_y$ in the middle diffraction pattern for the $(11\bar{1})$ peak (5.7(a)), the fringe spacing was sampled with 4 pixels, implying that reconstruction should be possible along the nanowire growth direction. However for $(\bar{1}\bar{1}1)$ (5.7(b)), the fringe spacing along $\vec{q}_y$ is not resolved, likely due to insufficient counts for this peak, meaning that if reconstruction is possible, the dimensions along the nanowire growth axis will not be well defined.

Considering again the $(11\bar{1})$ peak (5.7(a)), the fringe frequency along $\vec{q}_y$ is $\sim 0.012 \text{ nm}^{-1}$, corresponding to an object of length $\sim 520 \text{ nm}$. This is unexpected because NW-1 is $1.9 \text{ }\mu\text{m}$ as measured in SEM. Given this $1.9 \text{ }\mu\text{m}$ long nanowire and the $1.05 \text{ }\mu\text{m}$ height of the X-ray beam, a well defined fringe spacing along $\vec{q}_y$ is actually not expected. However, these fringes would not appear without the presence of a structurally isolated object $\sim 520 \text{ nm}$ in length within the nanowire. Because crystal phase and orientation of the GaAs core can change, we hypothesize that the 520 nm segment is bounded by structural defects that prevent the detection of scattering from other segments of the nanowire onto the CCD. Let us consider the sensitivity of the $\{11\bar{1}\}$ family to crystal phase. There is no equivalent WZ diffraction peak that aligns with the $\{11\bar{1}\}$, so WZ crystals will give zero intensity at this condition. However, at the given growth conditions, the GaAs cores are expected to be primarily of ZB structure. Within ZB, twin boundaries can occur, changing ABCABCABC stacking to CBACBACBA stacking, resulting

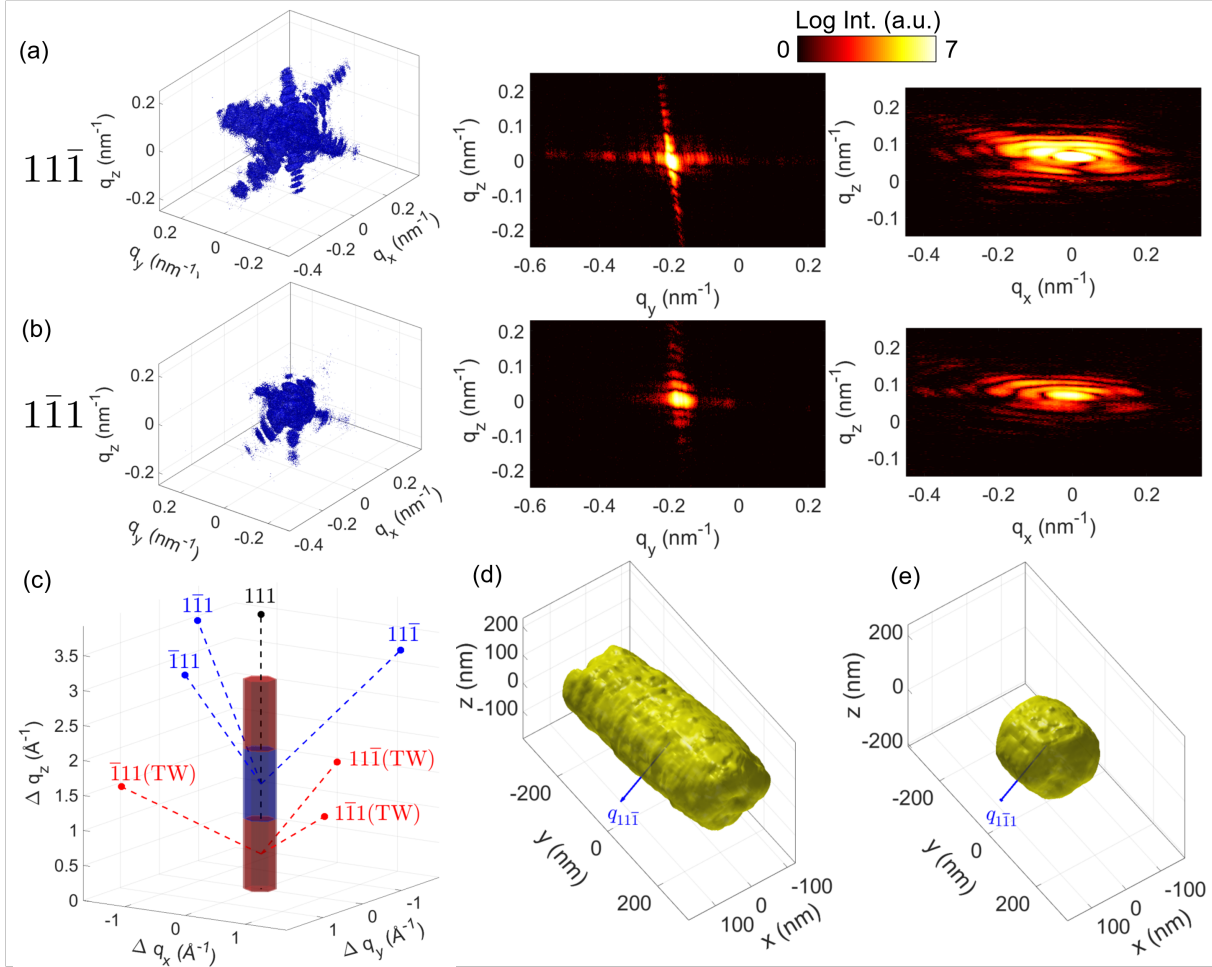


Figure 5.7. (a) 3D reciprocal space map (RSM) of diffraction (3 photon count isosurface) from the (111) condition of NW-1 (left). 2D cuts of this diffraction pattern on a log scale at the maximum intensity (center and right). (b) 3D RSM of diffraction (3 photon count isosurface) from the (111) condition of NW-1 (left). 2D cuts of this diffraction pattern on a log scale at the maximum intensity (center and right). (c) Reciprocal space map of vertical $\{111\}$ peaks for twinned and untwinned ZB, the twinned segment results in a 60° rotation of the $\{111\}$ putting them out of view of the detector. The twinned segment does not result in rotation of the (111) peak. (d) Isosurface of the support for the 3D reconstruction NW-1 at (111), with the q -vector labeled. (e) Isosurface of the support for the 3D reconstruction of NW-1 at (111), with the q -vector labeled. This segment is shorter because the fringes in the q_y direction of (111) are poorly defined.

in a change in the scattering condition. As shown in the schematic in Figure 5.7(c), for untwinned ZB (blue) there are three $\{111\}$ conditions that will scatter out of the substrate. However, upon twinning (red segment) these three $\{111\}$ peaks are rotated 60° . This schematic examples how twinned portions

of the ZB nanowire will scatter away from the detector (if the detector is aligned to an un-twinned ZB $\{11\bar{1}\}$ peak position). Thus we hypothesized that a small number of SFs within the nanowire result the crystallographic isolation of a ~ 520 nm segment of untwinned ZB embedded in the primarily twinned ZB nanowire. In support of this hypothesis, diffraction patterns collected from the (111) show no fringe structure along q_z , meaning that the crystal is unconstrained in that direction. This is expected when the nanowire does not fit within the beam vertically, as for NW-1, because the (111) condition is insensitive to rotational twins.

Since there was a fully crystallographically-isolated portion of untwinned ZB within the $1.05\text{ }\mu\text{m}$ beam, 3D reconstructions of this region were possible. Reconstructions were obtained using a combination of iterative phase retrieval algorithms in a Python module, developed by S. Maddali, which can be found on GitHub [433]. Specifically, 150 iterations of the phase retrieval algorithm Error Reduction (ER) were applied to an initial random guess of the 3D amplitudes and phases. Shrinkwrap was performed every 30 iterations. Hybrid input-output (HIO) error reduction was then applied for 300 iterations. Next, 100 iterations of Solvent Flipping was performed with shrinkwrap every 25 iterations, followed by another 300 HIO steps. Finally, 450 iterations of ER were applied with shrinkwrap every 90 iterations. The reconstruction process used in this work is well described in literature [434, 435], as are the error reduction algorithms [202, 203]. Reconstructions were performed 10 times for each diffraction peak using different initial random guesses. 2D/3D reconstructions shown in this work are from single reconstructions, but strain quantified in line plots is averaged from the best four reconstructions (lowest pixel by pixel cross-correlations), with error given by the variations between reconstructions. Given there are two solutions to the BCDI phase retrieval problem: $\rho(\mathbf{r})$ and $\rho^*(-\mathbf{r})$, the solution that most closely resembled the asymmetry in the QW structure was used since the nanowires were aligned in the beam with known orientation. Additionally, phase ramps were removed by centering the 3D diffraction patterns at the center voxel of the reconstruction grid.

Isosurfaces of the final object support from reconstructions of NW-1 for $(11\bar{1})$ and $(\bar{1}\bar{1}1)$ peaks are shown in Figure 5.7(d) and (e) respectively. The respective scattering vector (q) is shown in blue. For $(11\bar{1})$, the reconstruction is ~ 550 nm in length, similar to what was calculated in the previous section

from the fringe spacing in 5.7(a). A roughly hexagonal shape is seen in the cross-section with a diameter of ~ 210 nm in good agreement with SEM. For the $(1\bar{1}1)$ condition the reconstruction is also ~ 210 nm in diameter as expected. However, along the reconstructed nanowire length it is only ~ 220 nm, significantly shorter than in the $(11\bar{1})$ reconstruction. It is unlikely this is a different segment of untwinned material than in $(11\bar{1})$ (5.7(d)), because the $1.05 \mu\text{m}$ X-ray beam has an Airy tail that will span $4+ \mu\text{m}$ [202], so diffraction from a separate twinned segment would have some signal in the detector and reconstructions would not be possible for $(11\bar{1})$ or $(1\bar{1}1)$. As discussed previously, the low counts in the $(1\bar{1}1)$ diffraction peak makes it difficult to resolve the fringes along $\vec{q}_y$, so the nanowire long axis is poorly defined. The diffraction signal is still high enough to resolve the cross-sectional features of the nanowire. As such the length of the nanowire in 5.7(e) cannot be determined, and the twinned segment length should be considered as ~ 550 nm from the $(11\bar{1})$ reconstruction (5.7(d)). Note that this results in a reduced resolution along the real space y-dimension in the $(1\bar{1}1)$ reconstruction.

5.2.2.4. Strain analysis in reconstructed nanowires. While BCDI does not measure strain directly, instead measuring phase, the phases (ϕ_{hkl}) can be converted to a relative displacement field (u_{hkl}) of the hkl planes along the momentum vector (q_{hkl}) direction according to

$$(5.1) \quad u_{hkl} = \frac{\phi_{hkl}}{2\pi d_{hkl}}$$

where d_{hkl} is the unstrained lattice spacing of the hkl planes. This displacement field map can then be converted to relative strain along q_{hkl} by taking the spatial derivative

$$(5.2) \quad \epsilon_{hkl} = \frac{\delta u_{hkl}}{\delta x_{hkl}}$$

However, this is assuming that all phase features are a result of strain, which is not always the case. Other deviations in lattice structure such as defects will also modify the phase. As such, ‘strain’ maps discussed in the rest of this chapter may contain artifacts unrelated to strain.

For NW-1, cross-sectional cuts of the strain, $\epsilon_{1\bar{1}1}$ and $\epsilon_{11\bar{1}}$, are shown in Figure 5.8(c) and (e) respectively. Additionally, a longitudinal cross-section of $\epsilon_{11\bar{1}}$ is seen in 5.8(g), where the black dotted line is the location of the cut in (e). For reference, a schematic of the asymmetric nanowire structure is shown in 5.8(a) with $q_{11\bar{1}}$ and $q_{1\bar{1}1}$ directions marked. The q-vector is shown in purple in each strain cut, which is the direction of the strain component. For example, 5.8(c) shows the strain component $\epsilon_{1\bar{1}1}$, which

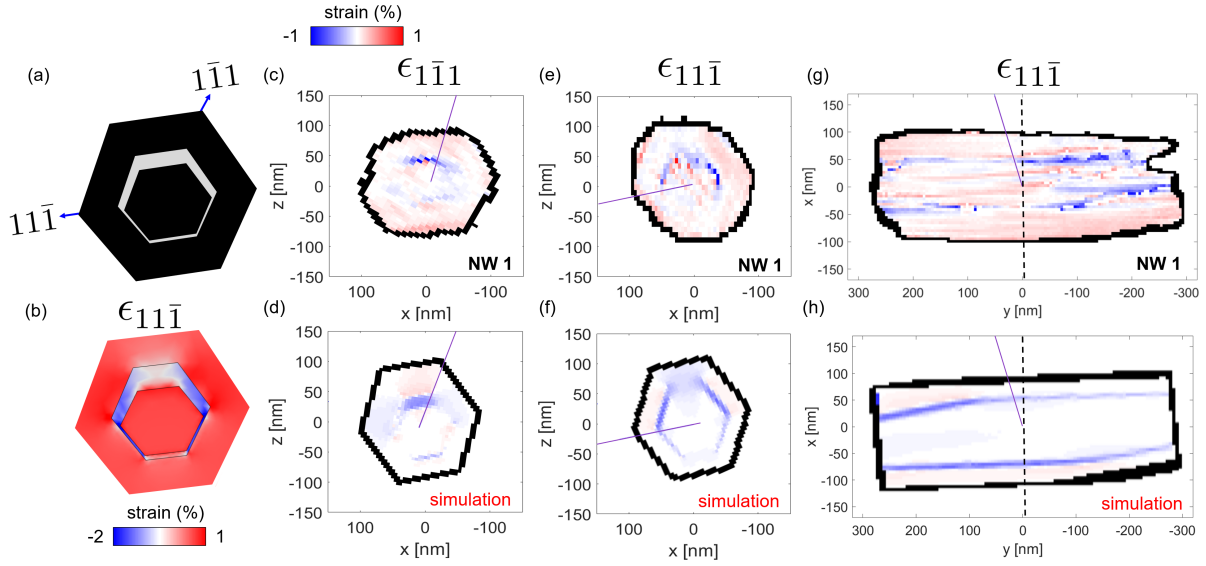


Figure 5.8. Experimental and simulated BCDI reconstructions for asymmetric QW heterostructures. (a) A schematic of the nominal nanowire heterostructure with the q-vectors for $(1\bar{1}\bar{1})$ and $(1\bar{1}\bar{1})$ shown for reference. (b) Strain output from COMSOL model of the structure in (a) with 20% In. (c) Cross-sectional cut of the $(1\bar{1}\bar{1})$ strain of NW-1 and the (d) corresponding simulated cut. (e) Cross-sectional cut of the $(1\bar{1}\bar{1})$ strain of NW-1 and the (f) corresponding simulated cut. (g) Longitudinal cross-section of the $(1\bar{1}\bar{1})$ strain of NW-1 and the (h) corresponding simulated cut. Note that the plotted strain range for (c-h) is -1% to 1%, compared to (b) which is -2% to 1%. All cross-sections are oriented as in (a).

maps the changes in strain in the planes perpendicular to the $[1\bar{1}\bar{1}]$ direction. Simulations of the strain were generated using finite element modeling in COMSOL, as described in Section 2.5.5. The nominal nanowire geometry shown in Figure 5.5(a) was used with an In content of 20%, resulting in a nominal lattice mismatch between InGaAs and GaAs of 1.79%. This nominal mismatch was used as the initial strain input for the InGaAs QW in the FEM simulation. The resulting strain field after relaxation for $\epsilon_{1\bar{1}\bar{1}}$ is seen in 5.5(b). This strain field shows a maximum of $\sim 2\%$ strain within the 2 nm QWs and $\sim 1\%$ strain within the 10 nm QWs. Displacement fields generated in COMSOL were then used in kinematic scattering simulations (also described in 2.5.5) using a plane-wave X-ray beam at conditions matching the experiment. Diffraction patterns were simulated, shot noise was added, and the resulting real space strain state reconstructed from these patterns is shown in Figure 5.8(d),(f), and (h). The simulated reconstructed strain maps show smaller variations in the strain field around the QW as compared to the

FEM simulation in Figure 5.8(b) because the simulations include the influence of detector pixel size on resolution; the strain the QW and the surrounding GaAs are convolved in the measurement. The simulated cross-sections in Figure 5.8(d),(f), and (h) correspond to the same conditions as the experimentally determined strains cuts in (c),(e), and (g) respectively. All cross-sectional cuts are oriented in the same fashion as the schematic in 5.8(a).

Aspects of the simulations and experiments are in agreement. A compressive field (blue) is shown around the thickest QW in 5.8(c), with a lower compressive strain in the region of the bottom facet (4 nm QW). In this scattering condition ($1\bar{1}1$), the q-vector is most sensitive to deviations in the 20 nm and 4 nm QWs because their growth facets, or interfaces with the GaAs matrix, are perpendicular to $\vec{q}$. At the other scattering condition ($11\bar{1}$) in 5.8(e),(g) the cross-section in (e) shows a compressive strain around the 10 nm QWs. In 5.8(g),(h), the longitudinal cuts show the same two bands of compressive strain due to the 10 nm QWs in the reconstruction and simulation. Again note that figure 5.8(c) and (e) derive from the same nanowire (NW-1), but plot different strain components; for $\epsilon_{11\bar{1}}$ (5.8(e)) the strain in and from the 20 nm QW is not evident because its planes are parallel to the $q_{11\bar{1}}$ vector, whereas this strain is resolved in $\epsilon_{1\bar{1}1}$ (5.8(c)).

Closer inspection of the simulations and measured reconstructions also reveals a few notable differences. First, for $\epsilon_{11\bar{1}}$ (5.8(e),(f)), the strain state in the 2 nm QWs is not readily evident in the experimental data like it is in the simulation. This is likely due to insufficient counting statistics in the experimental reconstruction, which makes it difficult to resolve such small spatial features. Further, the voxel size in the reconstruction is 4.9 nm, which determines the best possible resolution in the reconstruction (resolution will be different along the nanowire diameter and length); a 2 nm QW is therefore challenging to resolve. Second, also in $\epsilon_{11\bar{1}}$, the strain state appears to be higher in the right 10 nm QW than in the left, though they should be equal if the actual nanowire has the same symmetry as the schematic. Further, the longitudinal cut of $\epsilon_{11\bar{1}}$ contains numerous high strain features that fluctuate along the nanowire length (5.8(g),(h)). Finally, for $\epsilon_{1\bar{1}1}$ (5.8(c),(d)), the strain state in the 20 nm QW is higher than expected from the simulations. The strain in the QWs is investigated in more detail in Figure 5.9.

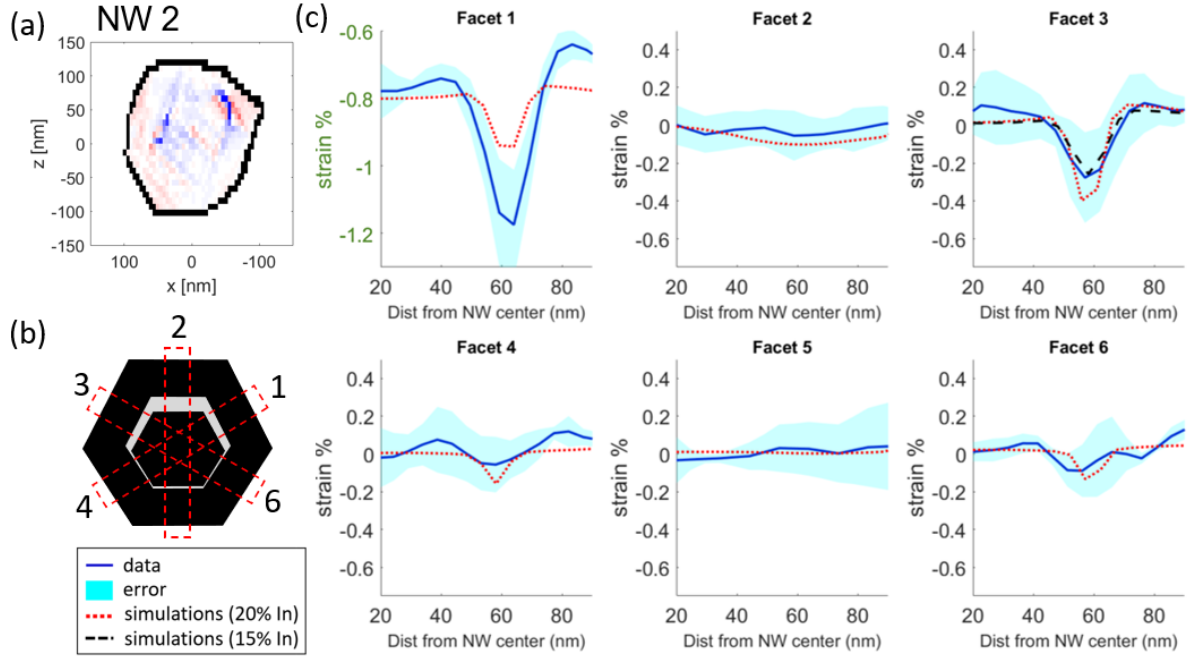


Figure 5.9. (a) The ϵ_{11} strain for NW-2. (b) Schematic of boxes in which line cuts were extracted, with nanowire facets labeled 1-6. (c) Line cuts for facets 1-6 showing the strain averaged between four reconstructions (blue) and the variance in strain between the reconstructions (light blue bands). Line cuts from the simulated strain for a nanowire of 20% In is overlaid (dotted red). For facet 3 the cut from simulations of 15% In are also shown (dashed black). Facet 1 is shown on a different strain scale than facets 2-6 (axis highlighted in green).

To sample other nanowires measured, the strain state ϵ_{11} is shown for a different nanowire (NW-2) in Figure 5.9(a). Similar strain features are revealed as in NW-1 (compared to Figure 5.8(e)), with compressive strain located in the region of the 10 nm QWs, but with higher strain within one of them. To investigate the strain in each QW in more detail, line profiles of average strain in each QW were taken by summing across a 20 pixel distance (~ 100 nm) in the center of the QW on each facet. Example boxes for the line profile extraction are shown in 5.9(b) and the facets are labeled 1-6. The line profiles are plotted outward from the nanowire core, as indicated by the red arrows in 5.9(b). Line plots were taken from facets 1-6 in four different reconstructions (random initial phase guess in the phase retrieval). The average of the four line plots at each facet are shown in 5.9(c). The error, or variance between the four line plots, is shown as a light blue band. Red dashed lines show the strain profiles extracted in the

same fashion from the COMSOL simulation. Facets 2 and 5 show no discernible strain in or around the QWs, in agreement with the simulation, since these profiles are extracted from the facets parallel to the scattering vector, $q_{1\bar{1}1}$. Facets 4 and 6, which correspond to the 2 nm QWs, show a small and broad dip in strain in the region of the QW. The strain magnitude matches the simulations of the 20% In content nanowire within experimental error, though the strain profile is broader in the experimental data. While the error (blue band) between reconstructions in facets 4 and 6 is large relative to the signal variation, the features are consistent with the expected strain variation due to a 2 nm QW. The ability to probe such small quantum features can be improved and made more reliable between reconstructions by increasing the exposure time or the angular range in the BCDI experiment. Finally, facets 1 and 3 correspond to the 10 nm QWs. Facet 3 shows a larger compressive strain than facets 4 and 6 as expected (line cuts from simulations of both 15% and 20% In content are shown in black and red, respectively). The 15% In QW simulation is a better match to the experiment, but the error in the reconstruction (denoted by the blue band) implies that the reconstruction is also consistent with a 20% In QW. Comparison of the error of the BCDI reconstruction with the simulations shows that for such small features, BCDI together with the assumption of strictly elastic relaxation cannot determine the In content with high accuracy. In future experiments, improved counting statistics (longer exposure) could be used to further constrain the reconstruction and reduce this variation. Facet 3 (10 nm QW) matches well with the simulations of a InGaAs QW with In content somewhere between 15 and 20 %. However, facet 1, the other 10 nm QW facet, shows a much larger compressive strain (almost 1.2%) than facet 3 (note the change in y-scale), and this compressive strain persists along the length of nanowire NW-2. The experimental results do not match the simulated strain profile for a nanowire with 20% In as represented by the red-dotted line. A similar deviation in strain was also seen in one of the 10 nm QWs and the 20 nm QW of NW-1, as shown in Figure 5.8(c)-(f).

5.2.2.5. Identification of individual defects using BCDI. Given the significant deviation in apparent strain between nominally identical 10 nm QWs in facets 1 and 3 in Figure 5.9(c), it is likely that defects make a significant contribution to the phase in the facet 1 reconstruction. For a qualitative understanding of how defects may manifest differently than strain gradients, it is useful to examine cross-sections of the

phase for NW-2 ($\phi_{11\bar{1}}$) and NW-1 ($\phi_{11\bar{1}}$ and $\phi_{1\bar{1}1}$) in Figure 5.10. Figure 5.10(a) shows the phase in NW-2 magnified in the region around facet 1 from Figure 5.9, which is qualitatively very different than the phase profile of the other 10 nm QW on the left side of the cross-section. Within the region outlined in red there is a clear phase wrap: from left to right the phase becomes more negative, then jumps from $-\pi$ to π across a single pixel, and then the phase moves again towards zero. Additionally, the lowest amplitude pixel (marked in white) within this cross-section is located at the core of this phase wrap. Similar features appear in NW-1 for both $\phi_{11\bar{1}}$ (5.10(b)) and $\phi_{1\bar{1}1}$ (5.10(d)) maps. This phase feature clearly deviates from the phase generated from simulations of strain, $\phi_{11\bar{1}}$ and $\phi_{1\bar{1}1}$ shown in 5.10(c) and (e) respectively. This type of phase wrap and the corresponding amplitude reduction has been observed previously during Bragg coherent diffraction imaging [213, 214, 215, 216] and was attributed to a screw or edge dislocation. The 2π phase ramps occur because dislocations cause displacement of atoms more than half a lattice distance from their equilibrium positions. This phase wrap behavior was observed for all 6 NWs at the corners of the 10 nm or 20 nm QWs.

Section 2.5.3 gave a brief discussion of incoherent growth in core-shell nanowires and noted that there is not a general model that predicts when dislocations will form nor type of dislocations that are most probable.[275, 274, 107] Qualitatively, defect formation is dependent on the core diameter, shell and barrier thicknesses, and lattice mismatch (In content). Yan et al. [107], predict critical InGaAs QW thicknesses for cylindrical nanowires with the same core/barrier thickness as studied in this work (100 nm GaAs core and 50 nm GaAs barrier). Their model predicts a critical QW thickness of ~ 13 nm for an analogous cylindrical structure at a 20% In content. Therefore, one would not expect defects to form in 2 or 4 nm QWs, but they would be likely to form in 20 nm QWs. Given the more complex geometry of the asymmetric QWs on an approximately hexagonal core, the influence of strain concentration on the location of defect formation should also be considered. The reconstructions based on BCDI exhibit phase wraps around the 10 nm and 20 nm QWs, with minimum amplitude values at the facet corners. This drop in amplitude has been linked to the location of the dislocation core, so the experimental data are consistent with the presence of dislocations at the corners of the 10 nm and 20 nm facets.

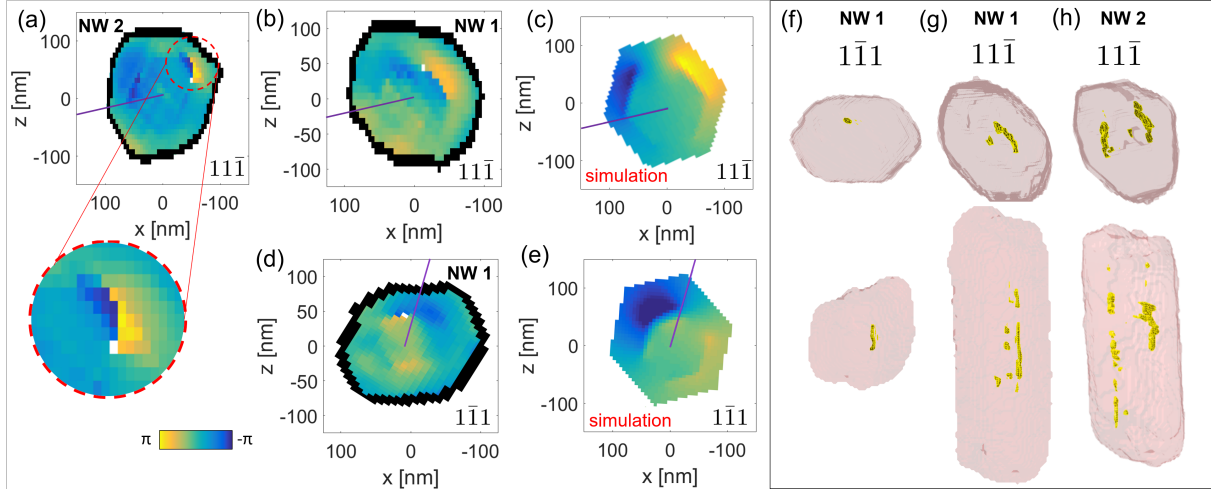


Figure 5.10. (a) The $(11\bar{1})$ phase of NW-2, with the region around the 10 nm QW magnified (facet 1 in 5.9(c)). (b) Phase map for $(11\bar{1})$ in NW-1. (c) Simulated $(11\bar{1})$ phase for 20% In nanowire. (d) Phase map for $(1\bar{1}1)$ in NW-1. (e) Simulated $(1\bar{1}1)$ phase for 20% In nanowire. Phase wraps are seen in the thickest facets for the experimental phases. The lowest amplitude pixel in each cut is marked in white, indicative of a dislocation core. (f-h) Mapping the 3D variations in the phase wrap, predicting the 3D dislocation core positions following the work of reference 216.

Pure screw dislocations due to shell misfit in nanowires are not predicted nor experimentally observed. Instead, either edge dislocation loops around the core or linear edge dislocations down the length of the nanowire are expected [275, 274]. Both of these types of edge dislocations have been observed via STEM in InAs-GaAs core-shell nanowires [436]. The possible extension of edge dislocations along the nanowire was probed using a min-max algorithm for tracking the presumed dislocation core, as described in reference 216. The algorithm calculates local minimum differentials in phase, and the pixels with differential values approaching the maximum (2π) are most likely situated around the dislocation core. A differential value of $4/3 \pi$ is plotted as an isosurface in yellow in Figure 5.10(f-h) for each scattering condition in NW-1 and NW-2. This differential cut off, which is the same as differential value used in reference 216, produces isosurfaces that extend along the growth axis. At the $(11\bar{1})$ condition, NW-1 (5.10(g)) shows an extended isosurface (predictive of a dislocation core) extending along the nanowire length. The isosurface segments are found at the corner connecting the 10 nm and 2 nm QWs on the right side, and to a lesser extent between the 10 nm and 20 nm QW on the right side. At the $(1\bar{1}1)$ condition for NW-1 (5.10(f)), an

additional core is resolved within the 20 nm QW (or at the 20 nm and 10 nm corner on the left side). As discussed previously, the $(1\bar{1}1)$ condition is poorly constrained along the NW length, so the resolution in that direction is limited. For NW-2 imaged in the $(11\bar{1})$ condition, 5.10(h), isosurface cores are seen at the corners of both 10 nm QWs and the 20 nm QW. For both nanowires, the dislocation cores predicted by the min-max calculation lie primarily along the length of the nanowire, which points to the presence of linear edge dislocations rather than loops. However, the dislocation cores are not fully continuous and do not extend along the entire nanowire length. This may be due to the limited experimental resolution, but it is also possible that defects are not present along the entire NW length due to changes in In content or QW width. Further discussion of the type of defect and the corresponding phase reconstruction that may occur due to defects is given in Appendix D. While the BCDI measurements give some information about the dislocation state in the nanowires, transmission electron microscopy appears to be necessary to confirm the presence, location, and identity of the dislocations within the nanowire QW structures analyzed here.

5.2.2.6. Summary and future work. Six asymmetric QW InGaAs/GaAs nanowires were imaged using BCDI at two diffraction conditions ($1\bar{1}1$ and $11\bar{1}$). These diffraction conditions probe primarily in-plane strain within the nanowire heterostructures. This is the first report of 3D BCDI reconstructions of in-plane strain in nanowires. The nanowires were imaged while standing vertically on the original Si growth substrate. Lithography and etching was used to remove the parasitic layer on the growth surface and the droplet on the top of the nanowires to prevent interference with the primary diffraction peak from the nanowire. Despite the fact that the nanowires that were longer than the coherent beam width, the presence low density ZB twinning is suggested to enable the 3D reconstruction of 500-600 nm untwinned segments. This use of ZB twinning as a boundary for crystallographic isolation of a nanowire segment for BCDI could be used in future experiments to investigate regions within extended nanowires. Since GaAs cores can be grown with precise control of the crystal phase [437], a nanowire core could be designed to have a single segment of twinned ZB that fits within the beam. The shell growth that follows will then adopt the same crystal structure. If this twinned segment is far from the droplet, the droplet may not need to be removed for 3D BCDI of the twinned portion. This unique approach for

crystallographic isolation of portions of a nanowire may eliminate the need for other types of processing, such as FIB milling, that can be damaging. Hence, the approach may enable measurements of nanowire samples previously thought not possible with BCDI.

Strain in two nanowires was analyzed in detail and compared to simulations. Simulated strains were determined via kinematic scattering simulations of nanowire displacement fields calculated in FEM. While the strain values varied up to $\sim 15\%$ between individual reconstructions from different starting guesses, the same strain features were consistently observed. The 2 nm facets showed a small ($< 0.2\%$) and broad dip in strain. Resolving features from the 2 nm QWs was limited by the spatial resolution of the BCDI measurement, which is typically 10-20 nm. This means that the reconstructed strain fields from the 2 nm QWs are broadened spatially, requiring comparison to kinematic scattering simulations to identify the strain state in the QW. While the apparent strain of some of the 10 nm facets was in good agreement with simulated strain, other 10 nm QWs and the 20 nm QW facet showed large deviations. The phase profile of NW-1 and NW-2 were shown to have large phase wraps and amplitude dips attributed to the presence of single dislocations. A differential phase algorithm was used to track the location of the predicted dislocation core through the nanowires in 3D. This algorithm identified potential dislocation cores extending down the length of the nanowires in both NW-1 and NW-2. This observation is consistent with the presence of linear edge dislocations at the interface of the core and the 10 and 20 nm QWs, which is reasonable given calculations of critical thicknesses for misfit dislocations in core-shell nanowires. Transmission electron microscopy measurements are suggested to confirm the presence of dislocations and identify their nature.

This experiment has identified a potential path for exploring the critical thicknesses of radial QWs in intact core-shell heterostructures. If nanowires are grown at different compositions and with variable QW thickness, this work suggests that BCDI can be used to associate the presence of single defects with particular locations in the heterostructure. Though time consuming, BCDI has a higher throughput than STEM measurements and does not require thinning, which could induce defects. BCDI of asymmetric radial QWs could therefore improve our understanding of misfit defects in nanowire heterostructures, particularly when correlated with electron microscopy.

CHAPTER 6

Outlook: Total Tomography for Characterizing Semiconductor Nanostructures

This thesis has demonstrated an approach to 3D correlative imaging, “total tomography”, for the purpose of extracting complex structure-property relationships in III-As nanowires. Several complementary nanoscale characterization techniques were employed to image the nanoscale variations in strain, crystal structure, and composition of quantum wells embedded in nanowires, and 3D imaging was often required to explain the optical or electrical properties. Further, direct correlation of multiple characterization techniques facilitated the interpretation of emission characteristics. This thesis also demonstrated numerous approaches to sample fabrication and design that allow for correlative imaging. One approach was the manipulation of specified nanowires for APT after spatially resolved CL mapping. Further, direct correlation between X-ray nanodiffraction and CL allowed for the correlation of strain, structure, and emission behavior. In the work described in Chapter 5.2, QW nanowires were grown and fabricated to enable in-plane CDI measurements of the nanowires in their epitaxial geometry. X-ray measurements in the as-grown geometry allowed for post-CDI measurements of emission using PL and will allow for the lift-out of the nanowires for APT or TEM analysis. These approaches to correlative, sometimes 3D characterization of single nanowires can be extended to analyze other nanowires or nanoscale heterostructures where strain, structure, or composition information is desired.

Beyond presenting multiple correlative tomographic analysis approaches, this thesis demonstrated advances in coherent X-ray imaging techniques that offer improvements in the analysis of 3D strain fields within nanostructures. A new approach to X-ray ptychographic strain imaging was introduced, maBPP, that allowed for the reconstruction of strain/structure with a spatial resolution of 2 and 50 nm. Further, CDI was used to image 3D strain in nanowires, resolving the in-plane strain field associated

with a 4 nm QW (10-20 nm spatial resolution). Many improvements can still be made to maBPP that would increase the spatial resolution and reliability in the reconstruction, such as correcting for error in the probe positions or angles within the phase retrieval algorithms. Use of DLSRs can also lead to improvements in coherent imaging techniques like CDI and maBPP. The increase in coherence length will allow for larger objects to be imaged with CDI. Additionally, the increase in coherent flux will increase the diffraction intensity, allowing for faster CDI or ptychography measurement or measurement of more weakly diffracting samples. DLSRs should be available to users on most continents by 2025, with two completed in Europe (MAX-IV, ESRF) and an upgrade of APS planned for 2022.

One major capability of X-ray imaging that was not utilized in this work is the *in operando* or *in situ* investigation of devices or materials. For example, the realization of compact III-As emitters for optical interconnects requires efficient electrically driven light emission. For electrical injection, metal contacts must be deposited on the nanowires and doping near the nanowire-metal interface is required to minimize contact resistance. This is a research area in which total tomography could play an important role. APT can be used to map the distribution of dopants, as demonstrated in Chapter 3. This analysis then could be indirectly correlated to measurements of the contact resistance between the nanowire and metal contact in order to optimize the doping conditions [438, 439]. Deposition of a metal contact will result in a stress applied on the nanowire heterostructure. This stress could result in strain within the nanowire in the region contacted with the metal, which can modify the band energy in this region. For example, a tensile strain of 3.5% has been shown to result in a 290 meV shift in GaAs/AlGaAs core/shell nanowires. [416, 105] The penetrating nature of CDI and X-ray ptychography means that the 3D strain state in the nanowire could be measured while it is embedded in the metal contact. Further, CDI or ptychography could also be performed *in operando* during electrical injection to investigate the effect of Joule heating on the nanowire strain and defect state.

Beyond investigation of III-V optical devices, total tomography, including the CDI or ptychography approaches used in this thesis can be extended to investigate structure property relationships in other nanowire devices. For example, in an extension of the finFET, researchers are pursuing gate-all-around (GAA) nanowires as a potential CMOS architecture. However, given the 3D nature of these devices,

total tomography is necessary to investigate interfacial mixing and strain between the Si/SiGe layers in the device. Both Si/Ge interfacial mixing and interfacial strain can modify the mobility of the carriers and the threshold voltage in the device. Further, non-uniform distribution of dopants can degrade the sub-threshold slope. Currently, EDS and GPA have been used to analyze composition and strain in GAA nanowires, but require milling of the nanowires at multiple orientations, providing only an indirect view of the 3D nature of these devices [440, 441]. Alternatively, APT correlated with CDI could be used to image the GAA nanowires in 3D. Though a test structure device would need to be fabricated, it is also possible that CDI could be used to directly correlate strain with mobility or threshold voltage in the GAA nanowire devices. Beyond nanowires devices, total tomography can be extended to other crystalline heterostructure devices that require investigation of strain, structure, or composition with high spatial resolution in three-dimensions. For instance, correlated X-ray ptychography and APT could be performed on polycrystalline thin films, such as photovoltaics or crystalline metal oxides of interest for solid-state batteries, to investigate the composition and strain state in individual nano/micro crystals in the films. This approach could allow for improved understanding of dopant distributions in polycrystalline films and interfacial strain between crystals that could lead to delamination during device operation.

Total tomography enables understanding of other important nanowire heterostructures such as those used in quantum computing. For instance, InAs nanowires grown on GaAs non-planar membranes are proposed as a support for topological qubits. The requirement for high mobility, defect-free, quasi-1D nanowires means that detailed understanding of doping, strain, and composition is critical [442, 443]. However, studying these nanostructures requires even higher spatial resolution than the InGaAs QW heterostructures investigated in this thesis. More generally, spatial resolution, chemical sensitivity, and need for 3D imaging are often limiting factors in characterizing nonplanar nanoscale heterostructures. However, continuous improvements, such as those discussed in this thesis, are being made to characterization techniques such as atom probe tomography, electron microscopy, and X-ray imaging. These advances are well-poised to elucidate the growth and properties in relevant nanoscale structures and ultimately enable the development of complex nanoscale devices with near atomic level precision.

Bibliography

- [1] W. M. Arden, “The International Technology Roadmap for Semiconductors—Perspectives and challenges for the next 15 years,” *Current Opinion in Solid State and Materials Science*, vol. 6, pp. 371–377, Oct. 2002.
- [2] B. Hoefflinger, “ITRS: The International Technology Roadmap for Semiconductors,” in *Chips 2020: A Guide to the Future of Nanoelectronics* (B. Hoefflinger, ed.), The Frontiers Collection, pp. 161–174, Berlin, Heidelberg: Springer, 2012.
- [3] S. Adachi, *Physical properties of III-V semiconductor compounds*. John Wiley & Sons, 1992.
- [4] J. W. Nicklas and J. W. Wilkins, “Accurate ab initio predictions of III–V direct-indirect band gap crossovers,” *Applied Physics Letters*, vol. 97, p. 091902, Aug. 2010.
- [5] A. Willner, *Optical Fiber Telecommunications*. Elsevier, May 2019.
- [6] J. J. Liou and W. W. Wong, “Comparison and optimization of the performance of Si and GaAs solar cells,” *Solar Energy Materials and Solar Cells*, vol. 28, pp. 9–28, Oct. 1992.
- [7] D. J. W. Flood, “Advanced Solar Cells for Satellite Power Systems,” tech. rep., Nov. 1994.
- [8] P. Komninou, J. Stoemenos, G. P. Dimitrakopoulos, and T. Karakostas, “Misfit dislocations and antiphase domain boundaries in GaAs/Si interface,” *Journal of Applied Physics*, vol. 75, pp. 143–152, Jan. 1994.
- [9] A. Georgakilas, J. Stoemenos, K. Tsagaraki, P. Komninou, N. Flevaris, P. Panayotatos, and A. Christou, “Generation and annihilation of antiphase domain boundaries in GaAs on Si grown by molecular beam epitaxy,” *Journal of Materials Research*, vol. 8, pp. 1908–1921, Aug. 1993.
- [10] K. Ishida, M. Akiyama, and S. Nishi, “Misfit and Threading Dislocations in GaAs Layers Grown on Si Substrates by MOCVD,” *Japanese Journal of Applied Physics*, vol. 26, p. L163, Mar. 1987.
- [11] Y. Itoh, T. Nishioka, A. Yamamoto, and M. Yamaguchi, “14.5% conversion efficiency GaAs solar cell fabricated on Si substrates,” *Applied Physics Letters*, vol. 49, pp. 1614–1616, Dec. 1986.
- [12] Y.-h. Lo, “Methods for growing defect-free heteroepitaxial layers,” Feb. 2001.
- [13] K. Tanabe, K. Watanabe, and Y. Arakawa, “III-V/Si hybrid photonic devices by direct fusion bonding,” *Scientific Reports*, vol. 2, pp. 1–6, Apr. 2012.
- [14] H. K. Choi, *Heteroepitaxy on Silicon: Fundamentals, Structure, and Devices: Symposium Held April 5-8, 1988, Reno, Nevada, USA*. Materials Research Society, 1988.
- [15] U. Gösele, Y. Bluhm, G. Kästner, P. Kopperschmidt, G. Kräuter, R. Scholz, A. Schumacher, S. Senz, Q.-Y. Tong, L.-J. Huang, Y.-L. Chao, and T. H. Lee, “Fundamental issues in wafer bonding,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 17, pp. 1145–1152, July 1999.
- [16] J. E. Bowers, D. Huang, D. Jung, J. Norman, M. A. Tran, Y. Wan, W. Xie, and Z. Zhang, “Realities and Challenges of III-V/Si Integration Technologies,” in *2019 Optical Fiber Communications Conference and Exhibition (OFC)*, pp. 1–3, Mar. 2019.
- [17] T. Mårtensson, C. P. T. Svensson, B. A. Wacaser, M. W. Larsson, W. Seifert, K. Deppert, A. Gustafsson, L. R. Wallenberg, and L. Samuelson, “Epitaxial III-V Nanowires on Silicon,” *Nano Letters*, vol. 4, pp. 1987–1990, Oct. 2004.

- [18] Y. Watanabe, H. Hibino, S. Bhunia, K. Tateno, and T. Sekiguchi, "Site-controlled InP nanowires grown on patterned Si substrates," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 24, pp. 133–137, Aug. 2004.
- [19] A. L. Roest, M. A. Verheijen, O. Wunnicke, S. Serafin, H. Wondergem, and E. P. A. M. Bakkers, "Position-controlled epitaxial III–V nanowires on silicon," *Nanotechnology*, vol. 17, pp. S271–S275, May 2006.
- [20] S.-G. Ihn, J.-I. Song, Y.-H. Kim, J. Y. Lee, and I.-H. Ahn, "Growth of GaAs Nanowires on Si Substrates Using a Molecular Beam Epitaxy," *IEEE Transactions on Nanotechnology*, vol. 6, pp. 384–389, May 2007. Conference Name: IEEE Transactions on Nanotechnology.
- [21] X.-Y. Bao, C. Soci, D. Susac, J. Bratvold, D. P. R. Aplin, W. Wei, C.-Y. Chen, S. A. Dayeh, K. L. Kavanagh, and D. Wang, "Heteroepitaxial Growth of Vertical GaAs Nanowires on Si (111) Substrates by Metal-Organic Chemical Vapor Deposition," *Nano Letters*, vol. 8, pp. 3755–3760, Nov. 2008.
- [22] G. Koblmüller, K. Vizbaras, S. Hertenberger, S. Bolte, D. Rudolph, J. Becker, M. Döbinger, M.-C. Amann, J. J. Finley, and G. Abstreiter, "Diameter Dependent Optical Emission Properties of InAs Nanowires grown on Si," *Appl. Phys. Lett.*, vol. 101, p. 053103, 2012.
- [23] G. Koblmüller, B. Mayer, T. Stettner, G. Abstreiter, and J. J. Finley, "GaAs–AlGaAs core–shell nanowire lasers on silicon: invited review," *Semiconductor Science and Technology*, vol. 32, no. 5, p. 053001, 2017.
- [24] W. Kern, *Thin Film Processes II*. Elsevier, Dec. 2012.
- [25] J. W. Dailey, J. Taraci, T. Clement, D. J. Smith, J. Drucker, and S. T. Picraux, "Vapor-liquid-solid growth of germanium nanostructures on silicon," *Journal of Applied Physics*, vol. 96, pp. 7556–7567, Dec. 2004.
- [26] J. C. Harmand, G. Patriarche, N. Péré-Laperne, M.-N. Mérat-Combes, L. Travers, and F. Glas, "Analysis of vapor-liquid-solid mechanism in Au-assisted GaAs nanowire growth," *Applied Physics Letters*, vol. 87, p. 203101, Nov. 2005.
- [27] Z. H. Wu, X. Y. Mei, D. Kim, M. Blumin, and H. E. Ruda, "Growth of Au-catalyzed ordered GaAs nanowire arrays by molecular-beam epitaxy," *Applied Physics Letters*, vol. 81, pp. 5177–5179, Dec. 2002.
- [28] A. J. Tavendale and S. J. Pearton, "Deep level, quenched-in defects in silicon doped with gold, silver, iron, copper or nickel," *Journal of Physics C: Solid State Physics*, vol. 16, pp. 1665–1673, Mar. 1983.
- [29] B. Bauer, A. Rudolph, M. Soda, A. F. i. Morral, J. Zweck, D. Schuh, and E. Reiger, "Position controlled self-catalyzed growth of GaAs nanowires by molecular beam epitaxy," *Nanotechnology*, vol. 21, p. 435601, Sept. 2010.
- [30] E. Galopin, L. Largeau, G. Patriarche, L. Travers, F. Glas, and J. C. Harmand, "Morphology of self-catalyzed GaN nanowires and chronology of their formation by molecular beam epitaxy," *Nanotechnology*, vol. 22, p. 245606, Apr. 2011.
- [31] S. Ambrosini, M. Fanetti, V. Grillo, A. Franciosi, and S. Rubini, "Vapor-liquid-solid and vapor-solid growth of self-catalyzed GaAs nanowires," *AIP Advances*, vol. 1, p. 042142, Nov. 2011.
- [32] J. Dufoule, C. Colombo, T. Garma, B. Ketterer, E. Uccelli, M. Nicotra, and A. Fontcuberta i Morral, "P-Doping Mechanisms in Catalyst-Free Gallium Arsenide Nanowires," *Nano Letters*, vol. 10, pp. 1734–1740, May 2010. Publisher: American Chemical Society.
- [33] S. Hertenberger, D. Rudolph, M. Bichler, J. J. Finley, G. Abstreiter, and G. Koblmüller, "Growth kinetics in position-controlled and catalyst-free InAs nanowire arrays on Si(111) grown by selective area molecular beam epitaxy," *Journal of Applied Physics*, vol. 108, p. 114316, Dec. 2010. Publisher: American Institute of Physics.

- [34] J. Noborisaka, J. Motohisa, and T. Fukui, "Catalyst-free growth of GaAs nanowires by selective-area metalorganic vapor-phase epitaxy," *Applied Physics Letters*, vol. 86, p. 213102, May 2005. Publisher: American Institute of Physics.
- [35] D. Rudolph, S. Hertenberger, S. Bolte, W. Paosangthong, D. Spirkoska, M. Döblinger, M. Bichler, J. J. Finley, G. Abstreiter, and G. Koblmüller, "Direct Observation of a Noncatalytic Growth Regime for GaAs Nanowires," *Nano Letters*, vol. 11, pp. 3848–3854, Sept. 2011. Publisher: American Chemical Society.
- [36] P. Aseev, A. Fursina, F. Boekhout, F. Krizek, J. E. Sestoft, F. Borsoi, S. Heedt, G. Wang, L. Binci, S. Martí-Sánchez, T. Swoboda, R. Koops, E. Uccelli, J. Arbiol, P. Krogstrup, L. P. Kouwenhoven, and P. Caroff, "Selectivity Map for Molecular Beam Epitaxy of Advanced III–V Quantum Nanowire Networks," *Nano Letters*, vol. 19, pp. 218–227, Jan. 2019.
- [37] M. Je, S. Han, I. Kim, and H. Shin, "A silicon quantum wire transistor with one-dimensional subband effects," *Solid-State Electronics*, vol. 44, pp. 2207–2212, Dec. 2000.
- [38] T. Sugaya, J. P. Bird, M. Ogura, Y. Sugiyama, D. K. Ferry, and K.-Y. Jang, "Quantum-interference characteristics of a 25 nm trench-type InGaAs/InAlAs quantum-wire field-effect transistor," *Applied Physics Letters*, vol. 80, pp. 434–436, Jan. 2002.
- [39] S. Bangsaruntip, G. M. Cohen, S. Narasimha, and J. W. Sleight, "Planar and nanowire field effect transistors," June 2013.
- [40] H.-J. Choi, J. C. Johnson, R. He, S.-K. Lee, F. Kim, P. Pauzauskie, J. Goldberger, R. J. Saykally, and P. Yang, "Self-Organized GaN Quantum Wire UV Lasers," *The Journal of Physical Chemistry B*, vol. 107, pp. 8721–8725, Aug. 2003.
- [41] E. Kapon, S. Simhony, R. Bhat, and D. M. Hwang, "Single quantum wire semiconductor lasers," *Applied Physics Letters*, vol. 55, pp. 2715–2717, Dec. 1989.
- [42] P. J. Pearah, E. M. Stellini, A. C. Chen, A. M. Moy, K. C. Hsieh, and K. Y. Cheng, "Strained GaIn_{1-x}P multiple quantum wire light-emitting diodes: A luminescence polarization study," *Applied Physics Letters*, vol. 62, pp. 729–731, Feb. 1993.
- [43] T. D. Stanescu and S. Tewari, "Majorana fermions in semiconductor nanowires: fundamentals, modeling, and experiment," *Journal of Physics: Condensed Matter*, vol. 25, p. 233201, May 2013.
- [44] M. d. la Mata, X. Zhou, F. Furtmayr, J. Teubert, S. Gradečák, M. Eickhoff, A. F. i. Morral, and J. Arbiol, "A review of MBE grown 0D, 1D and 2D quantum structures in a nanowire," *Journal of Materials Chemistry C*, vol. 1, no. 28, pp. 4300–4312, 2013.
- [45] N. Jeon, B. Loitsch, S. Morkötter, G. Abstreiter, J. Finley, H. J. Krenner, G. Koblmüller, and L. J. Lauhon, "Alloy Fluctuations Act as Quantum Dot-like Emitters in GaAs-AlGaAs Core-Shell Nanowires," *ACS Nano*, vol. 9, p. 8335, 2015.
- [46] L. Mancini, Y. Fontana, S. Conesa-Boj, I. Blum, F. Vurpillot, L. Francaviglia, E. Russo-Averchi, M. Heiss, J. Arbiol, A. F. i. Morral, and L. Rigutti, "Three-dimensional nanoscale study of Al segregation and quantum dot formation in GaAs/AlGaAs core-shell nanowires," *Applied Physics Letters*, vol. 105, p. 243106, Dec. 2014.
- [47] T. Stettner, T. Kostenbader, D. Ruhstorfer, J. Bissinger, H. Riedl, M. Kaniber, G. Koblmüller, and J. J. Finley, "Direct Coupling of Coherent Emission from Site-Selectively Grown III–V Nanowire Lasers into Proximal Silicon Waveguides," *ACS Photonics*, vol. 4, pp. 2537–2543, Oct. 2017.
- [48] L. C. Chuang, F. G. Sedgwick, R. Chen, W. S. Ko, M. Moewe, K. W. Ng, T.-T. D. Tran, and C. Chang-Hasnain, "GaAs-Based Nanoneedle Light Emitting Diode and Avalanche Photodiode Monolithically Integrated on a Silicon Substrate," *Nano Letters*, vol. 11, pp. 385–390, Feb. 2011.
- [49] X. Yan, X. Zhang, J. Li, Y. Wu, J. Cui, and X. Ren, "Fabrication and optical properties of GaAs/InGaAs/GaAs nanowire core-multishell quantum well heterostructures," *Nanoscale*, vol. 7, no. 3, pp. 1110–1115, 2015.

- [50] E. Dimakis, U. Jahn, M. Ramsteiner, A. Tahraoui, J. Grandal, X. Kong, O. Marquardt, A. Trampert, H. Riechert, and L. Geelhaar, "Coaxial Multishell (In,Ga)As/GaAs Nanowires for Near-Infrared Emission on Si Substrates," *Nano Letters*, vol. 14, pp. 2604–2609, May 2014.
- [51] T. Stettner, P. Zimmermann, B. Loitsch, M. Döblinger, A. Regler, B. Mayer, J. Winnerl, S. Matich, H. Riedl, M. Kaniber, G. Abstreiter, G. Koblmüller, and J. J. Finley, "Coaxial GaAs-AlGaAs core-multishell nanowire lasers with epitaxial gain control," *Applied Physics Letters*, vol. 108, p. 011108, Jan. 2016.
- [52] Y. Arakawa and H. Sakaki, "Multidimensional quantum well laser and temperature dependence of its threshold current," *Applied Physics Letters*, vol. 40, pp. 939–941, June 1982.
- [53] M. E. Hoenk, C. W. Nieh, H. Z. Chen, and K. J. Vahala, "Compositional modulation in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers grown by molecular beam epitaxy on the (111) facets of grooves in a nonplanar substrate," *Applied Physics Letters*, vol. 55, pp. 53–55, July 1989.
- [54] K. A. Mäder and A. Zunger, "Effects of atomic clustering on the optical properties of III-V alloys," *Applied Physics Letters*, vol. 64, pp. 2882–2884, May 1994.
- [55] B. Loitsch, N. Jeon, M. Döblinger, J. Winnerl, E. Parzinger, S. Matich, U. Wurstbauer, H. Riedl, G. Abstreiter, J. J. Finley, L. J. Lauhon, and G. Koblmüller, "Suppression of alloy fluctuations in GaAs-AlGaAs core-shell nanowires," *Applied Physics Letters*, vol. 109, p. 093105, Aug. 2016.
- [56] J. C. Mikkelsen and J. B. Boyce, "Extended x-ray-absorption fine-structure study of $\{\text{Ga}\}_{1-x}\{\text{In}\}_x\text{As}$ random solid solutions," *Physical Review B*, vol. 28, pp. 7130–7140, Dec. 1983.
- [57] F. Glas, C. Gors, and P. Hénoc, "Diffuse scattering, size effect and alloy disorder in ternary and quaternary III-V compounds," *Philosophical Magazine B*, vol. 62, pp. 373–394, Oct. 1990.
- [58] D. Rudolph, D. Funk, Stefan, Markus, S. Morkötter, S. Hertenberger, L. Schweickert, J. Becker, S. Matich, M. Bichler, and D. Spirkoska, "Spontaneous alloy composition ordering in GaAs-AlGaAs core-shell nanowires," *Nano Lett.*, vol. 13, no. 4, pp. 1522–1527. DOI: 10.1021/nl3046816, 2013. tex.publisher: ACS Publications.
- [59] Q. Zhang, P. W. Voorhees, and S. H. Davis, "Mechanisms of surface alloy segregation on faceted core-shell nanowire growth," *Journal of the Mechanics and Physics of Solids*, vol. 100, pp. 21–44, Mar. 2017.
- [60] C. Zheng, J. Wong-Leung, Q. Gao, H. H. Tan, C. Jagadish, and J. Etheridge, "Polarity-Driven 3-Fold Symmetry of GaAs/AlGaAs Core Multishell Nanowires," *Nano Letters*, vol. 13, pp. 3742–3748, Aug. 2013.
- [61] D. Rudolph, L. Schweickert, S. Morkötter, L. Hanschke, S. Hertenberger, M. Bichler, G. Koblmüller, G. Abstreiter, and J. J. Finley, "Probing the trapping and thermal activation dynamics of excitons at single twin defects in GaAs-AlGaAs core-shell nanowires," *New Journal of Physics*, vol. 15, p. 113032, Nov. 2013.
- [62] E. F. Schubert, *Doping in III-V Semiconductors*, *Cambridge Studies in Semiconductor Physics and Microelectronics Engineering*. 1993.
- [63] P. M. Mooney, "Donor-related levels in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$," *Semiconductor Science and Technology*, vol. 6, pp. B1–B8, Oct. 1991.
- [64] P. Vaccaro, "Epitaxial growth and amphoteric doping on GaAs (n11)A-oriented substrates," in *Conference Proceedings. 2001 International Conference on Indium Phosphide and Related Materials. 13th IPRM (Cat. No.01CH37198)*, pp. 47–50, May 2001.
- [65] M. J. Ashwin, M. R. Fahy, R. C. Newman, J. Wagner, D. A. Robbie, M. J. L. Sangster, I. Silier, E. Bauser, W. Braun, and K. Ploog, "A local vibrational mode investigation of p -type Si-doped GaAs," *Journal of Applied Physics*, vol. 76, pp. 7839–7849, Dec. 1994.
- [66] Y. Diao, L. Liu, and S. Xia, "Exploration the p -type doping mechanism of GaAs nanowires from first-principles study," *Physics Letters A*, vol. 383, pp. 202–209, Jan. 2019.

- [67] R. Heckingbottom and G. J. Davies, "Germanium doping of gallium arsenide grown by molecular beam epitaxy — Some thermodynamic aspects," *Journal of Crystal Growth*, vol. 50, pp. 644–647, Nov. 1980.
- [68] J. Wallentin and M. T. Borgström, "Doping of semiconductor nanowires," *Journal of Materials Research*, vol. 26, pp. 2142–2156, Sept. 2011. Publisher: Cambridge University Press.
- [69] J. G. Connell, K. Yoon, D. E. Perea, E. J. Schwalbach, P. W. Voorhees, and L. J. Lauhon, "Identification of an Intrinsic Source of Doping Inhomogeneity in Vapor–Liquid–Solid-Grown Nanowires," *Nano Letters*, vol. 13, pp. 199–206, Jan. 2013.
- [70] W. Chen, V. G. Dubrovskii, X. Liu, T. Xu, R. Lardé, J. Philippe Nys, B. Grandidier, D. Stiévenard, G. Patriarche, and P. Pareige, "Boron distribution in the core of Si nanowire grown by chemical vapor deposition," *Journal of Applied Physics*, vol. 111, p. 094909, May 2012.
- [71] M. H. T. Dastjerdi, E. M. Fiordaliso, E. D. Leshchenko, A. Akhtari-Zavareh, T. Kasama, M. Aagesen, V. G. Dubrovskii, and R. R. LaPierre, "Three-fold Symmetric Doping Mechanism in GaAs Nanowires," *Nano Letters*, vol. 17, pp. 5875–5882, Oct. 2017.
- [72] L. Rigutti, A. De Luna Bugallo, M. Tchernycheva, G. Jacopin, F. H. Julien, G. Cirlin, G. Patriarche, D. Lucot, L. Travers, and J.-C. Harmand, "Si Incorporation in InP Nanowires Grown by Au-Assisted Molecular Beam Epitaxy," 2009.
- [73] A. Casadei, P. Krogstrup, M. Heiss, J. A. Röhr, C. Colombo, T. Ruelle, S. Upadhyay, C. B. Sørensen, J. Nygård, and A. Fontcuberta i Morral, "Doping incorporation paths in catalyst-free Be-doped GaAs nanowires," *Applied Physics Letters*, vol. 102, p. 013117, Jan. 2013.
- [74] C.-Y. Yeh, Z. W. Lu, S. Froyen, and A. Zunger, "Zinc-blende–wurtzite polytypism in semiconductors," *Physical Review B*, vol. 46, pp. 10086–10097, Oct. 1992.
- [75] L. Rigutti, "Semiconductor Nanowires," in *Wiley Encyclopedia of Electrical and Electronics Engineering*, pp. 1–33, American Cancer Society, 2015.
- [76] P. Caroff, J. Bolinsson, and J. Johansson, "Crystal Phases in III–V Nanowires: From Random Toward Engineered Polytypism," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 17, pp. 829–846, July 2011. Citation Key Alias: Carof_2011.
- [77] M. A. Verheijen, R. E. Algra, M. T. Borgström, G. Immink, E. Sourty, W. J. van Enkevort, E. Vlieg, and E. P. Bakkers, "Three-dimensional morphology of GaP–GaAs nanowires revealed by transmission electron microscopy tomography," *Nano Lett.*, vol. 7, no. 10, pp. 3051–3055. DOI: 10.1021/nl071541q, 2007. tex.publisher: ACS Publications.
- [78] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M. Gass, A. L. Bleloch, and S. Estrade, "Structural and optical properties of high quality zinc-blende/wurtzite GaAs nanowire heterostructures," *Phys. Rev. B*, vol. 80, no. 24, p. 245325. DOI: 10.1103/PhysRevB.80.245325, 2009. tex.publisher: APS.
- [79] M. Yamaguchi, J.-H. Paek, and H. Amano, "Probability of twin formation on self-catalyzed GaAs nanowires on Si substrate," *Nanoscale Research Letters*, vol. 7, p. 558, Oct. 2012.
- [80] P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert, and L. Samuelson, "Controlled polytypic and twin-plane superlattices in iii–v nanowires," *Nature Nanotechnology*, vol. 4, pp. 50–55, Jan. 2009.
- [81] F. Glas, J.-C. Harmand, and G. Patriarche, "Why Does Wurtzite Form in Nanowires of III-V Zinc Blende Semiconductors?," *Physical Review Letters*, vol. 99, p. 146101, Oct. 2007.
- [82] G. E. Cirlin, V. G. Dubrovskii, Y. B. Samsonenko, A. D. Bouravleuv, K. Durose, Y. Y. Proskuryakov, B. Mendes, L. Bowen, M. A. Kaliteevski, R. A. Abram, and D. Zeze, "Self-catalyzed, pure zincblende GaAs nanowires grown on Si(111) by molecular beam epitaxy," *Physical Review B*, vol. 82, p. 035302, July 2010.
- [83] A. S. Ameruddin, H. A. Fonseka, P. Caroff, J. Wong-Leung, R. L. O. h. Veld, J. L. Boland, M. B. Johnston, H. H. Tan, and C. Jagadish, "In_xGa_{1-x}As nanowires with uniform composition, pure

- wurtzite crystal phase and taper-free morphology,” *Nanotechnology*, vol. 26, p. 205604, Apr. 2015.
- [84] E. Gil, V. G. Dubrovskii, G. Avit, Y. André, C. Leroux, K. Lekhal, J. Grecenkov, A. Trassoudaine, D. Castelluci, G. Monier, R. M. Ramdani, C. Robert-Goumet, L. Bideux, J. C. Harmand, and F. Glas, “Record Pure Zincblende Phase in GaAs Nanowires down to 5 nm in Radius,” *Nano Letters*, vol. 14, pp. 3938–3944, July 2014.
 - [85] T. Grap, T. Rieger, C. Blömers, T. Schäpers, D. Grützmacher, and M. I. Lepsa, “Self-catalyzed VLS grown InAs nanowires with twinning superlattices,” *Nanotechnology*, vol. 24, p. 335601, July 2013.
 - [86] T. Rieger, M. I. Lepsa, T. Schäpers, and D. Grützmacher, “Controlled wurtzite inclusions in self-catalyzed zinc blende III–V semiconductor nanowires,” *Journal of Crystal Growth*, vol. 378, pp. 506–510, Sept. 2013.
 - [87] N. Vainorius, S. Kubitz, S. Lehmann, L. Samuelson, K. A. Dick, and M.-E. Pistol, “Temperature dependent electronic band structure of wurtzite GaAs nanowires,” *Nanoscale*, vol. 10, no. 3, pp. 1481–1486, 2018.
 - [88] A. Senichev, P. Corfdir, O. Brandt, M. Ramsteiner, S. Breuer, J. Schilling, L. Geelhaar, and P. Werner, “Electronic properties of wurtzite GaAs: A correlated structural, optical, and theoretical analysis of the same polytypic GaAs nanowire,” *Nano Research*, vol. 11, pp. 4708–4721, Sept. 2018.
 - [89] L. Ahtapodov, J. Todorovic, P. Olk, T. Mjåland, P. Slåttnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, “A Story Told by a Single Nanowire: Optical Properties of Wurtzite GaAs,” *Nano Letters*, vol. 12, pp. 6090–6095, Dec. 2012.
 - [90] S. Morkötter, S. Funk, M. Liang, M. Döblinger, S. Hertenberger, J. Treu, D. Rudolph, A. Yadav, J. Becker, M. Bichler, G. Scarpa, P. Lugli, I. Zardo, J. J. Finley, G. Abstreiter, and G. Koblmüller, “Role of microstructure on optical properties in high-uniformity In_{0.1}Ga_{0.9}As nanowire arrays: Evidence of a wider wurtzite band gap,” *Physical Review B*, vol. 87, p. 205303, May 2013. Publisher: American Physical Society.
 - [91] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M. H. Gass, A. L. Bleloch, S. Estrade, M. Kaniber, J. Rossler, F. Peiro, J. R. Morante, G. Abstreiter, L. Samuelson, and A. Fontcuberta i Morral, “Structural and optical properties of high quality zinc-blende/wurtzite GaAs nanowire heterostructures,” *Physical Review B*, vol. 80, p. 245325, Dec. 2009.
 - [92] N. Vainorius, D. Jacobsson, S. Lehmann, A. Gustafsson, K. A. Dick, L. Samuelson, and M.-E. Pistol, “Observation of type-II recombination in single wurtzite/zinc-blende GaAs heterojunction nanowires,” *Physical Review B*, vol. 89, p. 165423, Apr. 2014.
 - [93] R. Gurwitz, A. Tavor, L. Karpeles, I. Shalish, W. Yi, G. Seryogin, and V. Narayanamurti, “Bandgap and band discontinuity in wurtzite/zincblende GaAs homomaterial heterostructure,” *Applied Physics Letters*, vol. 100, p. 191602, May 2012.
 - [94] A. M. Graham, P. Corfdir, M. Heiss, S. Conesa-Boj, E. Uccelli, A. Fontcuberta i Morral, and R. T. Phillips, “Exciton localization mechanisms in wurtzite/zinc-blende GaAs nanowires,” *Physical Review B*, vol. 87, Mar. 2013.
 - [95] B. Loitsch, J. Winnerl, G. Grimaldi, J. Wierzbowski, D. Rudolph, S. Morkötter, M. Döblinger, G. Abstreiter, G. Koblmüller, and J. J. Finley, “Crystal phase quantum dots in the ultrathin core of GaAs–AlGaAs core–shell nanowires,” *Nano letters*, vol. 15, no. 11, pp. 7544–7551. DOI:10.1021/acs.nanolett.5b03273, 2015. tex.publisher: ACS Publications.
 - [96] H. M. Otte and A. G. Crocker, “Crystallographic Formulae for Hexagonal Lattices,” *physica status solidi (b)*, vol. 9, no. 2, pp. 441–450, 1965.
 - [97] F. C. Frank, “On Miller–Bravais indices and four-dimensional vectors,” *Acta Crystallographica*, vol. 18, pp. 862–866, May 1965.

- [98] G. Koblmüller, B. Mayer, T. Stettner, G. Abstreiter, and J. J. Finley, “GaAs-AlGaAs core-shell nanowire lasers on silicon: invited review,” *Semicond. Sci. Tech.*, vol. 32, no. 5, pp. 053001. DOI: 10.1088/1361-6641/aa5e45, 2017.
- [99] B. Mayer, D. Rudolph, J. Schnell, S. Morkötter, J. Winnerl, J. Treu, K. Müller, G. Bracher, G. Abstreiter, G. Koblmüller, and J. J. Finley, “Lasing from individual GaAs-AlGaAs core-shell nanowires up to room temperature,” *Nature Communications*, vol. 4, pp. 1–7, Dec. 2013.
- [100] M. Heiß, A. Gustafsson, S. Conesa-Boj, F. Peiró, J. R. Morante, G. Abstreiter, J. Arbiol, L. Samuelson, and A. F. i. Morral, “Catalyst-free nanowires with axial $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ heterostructures,” *Nanotechnology*, vol. 20, p. 075603, Jan. 2009.
- [101] M. Heiss, S. Conesa-Boj, J. Ren, H.-H. Tseng, A. Gali, A. Rudolph, E. Uccelli, F. Peiró, J. R. Morante, D. Schuh, E. Reiger, E. Kaxiras, J. Arbiol, and A. Fontcuberta i Morral, “Direct correlation of crystal structure and optical properties in wurtzite/zinc-blende GaAs nanowire heterostructures,” *Physical Review B*, vol. 83, p. 045303, Jan. 2011.
- [102] S. Hertenberger, D. Rudolph, J. Becker, M. Bichler, J. J. Finley, G. Abstreiter, and G. Koblmüller, “Rate Limiting Mechanisms in High-temperature Growth of Catalyst-free InAs Nanowires with Large Thermal Stability,” *Nanotechnology*, vol. 23, p. 235602, 2012.
- [103] J. Treu, M. Speckbacher, K. Saller, S. Morkötter, M. Döblinger, X. Xu, H. Riedl, G. Abstreiter, J. Finley, and G. Koblmüller, “Widely tunable alloy composition and crystal structure in catalyst-free InGaAs nanowire arrays grown by selective area molecular beam epitaxy,” *Appl. Phys. Lett.*, vol. 108, no. 5, p. 053110. DOI: 10.1063/1.4941407, 2016. tex.publisher: AIP Publishing.
- [104] S. W. Eaton, A. Fu, A. B. Wong, C.-Z. Ning, and P. Yang, “Semiconductor nanowire lasers,” *Nature Reviews Materials*, vol. 1, pp. 1–11, May 2016.
- [105] L. Balaghi, G. Bussone, R. Grifone, R. Hübner, J. Grenzer, M. Ghorbani-Asl, A. V. Krashennnikov, H. Schneider, M. Helm, and E. Dimakis, “Widely tunable GaAs bandgap via strain engineering in core/shell nanowires with large lattice mismatch,” *Nature Communications*, vol. 10, p. 2793, June 2019.
- [106] K. L. Kavanagh, I. Saveliev, M. Blumin, G. Swadener, and H. E. Ruda, “Faster radial strain relaxation in InAs–GaAs core–shell heterowires,” *Journal of Applied Physics*, vol. 111, p. 044301, Feb. 2012.
- [107] X. Yan, S. Fan, X. Zhang, and X. Ren, “Analysis of Critical Dimensions for Nanowire Core-Multishell Heterostructures,” *Nanoscale Research Letters*, vol. 10, p. 389, Oct. 2015.
- [108] J. Grandal, M. Wu, X. Kong, M. Hanke, E. Dimakis, L. Geelhaar, H. Riechert, and A. Trampert, “Plan-view transmission electron microscopy investigation of GaAs/(In,Ga)As core-shell nanowires,” *Applied Physics Letters*, vol. 105, p. 121602, Sept. 2014.
- [109] C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander, “Effect of strain on surface morphology in highly strained InGaAs films,” *Physical Review Letters*, vol. 66, pp. 3032–3035, June 1991.
- [110] R. Gargallo-Caballero, E. Luna, F. Ishikawa, and A. Trampert, “Strain-induced composition limitation in nitrogen δ -doped (In,Ga)As/GaAs quantum wells,” *Applied Physics Letters*, vol. 100, p. 171906, Apr. 2012.
- [111] P. R. C. Kent, G. L. W. Hart, and A. Zunger, “Biaxial strain-modified valence and conduction band offsets of zinc-blende GaN, GaP, GaAs, InN, InP, and InAs, and optical bowing of strained epitaxial InGaN alloys,” *Applied Physics Letters*, vol. 81, pp. 4377–4379, Nov. 2002.
- [112] T. Cheiwchanchamnangij and W. R. L. Lambrecht, “Band structure parameters of wurtzite and zinc-blende GaAs under strain in the GW approximation,” *Physical Review B*, vol. 84, July 2011.
- [113] I. J. Fritz, T. J. Drummond, G. C. Osbourn, J. E. Schirber, and E. D. Jones, “Electrical transport of holes in GaAs/InGaAs/GaAs single strained quantum wells,” *Applied Physics Letters*, vol. 48, pp. 1678–1680, June 1986.

- [114] D. J. Arent, K. Deneffe, C. Van Hoof, J. De Boeck, and G. Borghs, "Strain effects and band offsets in GaAs/InGaAs strained layered quantum structures," *Journal of Applied Physics*, vol. 66, pp. 1739–1747, Aug. 1989.
- [115] T. Omori, Y. Kurihara, Y. Takeuchi, M. Yoshioka, T. Nakanishi, S. Okumi, M. Tsubata, M. Tawada, K. Togawa, Y. Tanimoto, C. Takahashi, T. Baba, and M. Mizuta, "Highly Polarized Electron Source Using InGaAs–GaAs Strained-Layer Superlattice," *Japanese Journal of Applied Physics*, vol. 33, p. 5676, Oct. 1994.
- [116] J. C. Shin, K. H. Kim, K. J. Yu, H. Hu, L. Yin, C.-Z. Ning, J. A. Rogers, J.-M. Zuo, and X. Li, "In_xGa_{1-x}As Nanowires on Silicon: One-Dimensional Heterogeneous Epitaxy, Bandgap Engineering, and Photovoltaics," *Nano Letters*, vol. 11, pp. 4831–4838, Nov. 2011.
- [117] F. Vietmeyer, M. P. McDonald, and M. Kuno, "Single Nanowire Microscopy and Spectroscopy," *The Journal of Physical Chemistry C*, vol. 116, pp. 12379–12396, June 2012.
- [118] A. Maharjan, K. Pemasiri, P. Kumar, A. Wade, L. M. Smith, H. E. Jackson, J. M. Yarrison-Rice, A. Kogan, S. Paiman, Q. Gao, H. H. Tan, and C. Jagadish, "Room temperature photocurrent spectroscopy of single zincblende and wurtzite InP nanowires," *Applied Physics Letters*, vol. 94, p. 193115, May 2009.
- [119] R. Erdélyi, M. Hannibal Madsen, G. Sáfrán, Z. Hajnal, I. Endre Lukács, G. Fülöp, S. Csonka, J. Nygård, and J. Volk, "In-situ mechanical characterization of wurtzite InAs nanowires," *Solid State Communications*, vol. 152, pp. 1829–1833, Oct. 2012.
- [120] Y. Peng, I. Luxmoore, M. D. Forster, A. G. Cullis, and B. J. Inkson, "Nanomanipulation and electrical behaviour of a single gold nanowire using in-situ SEM-FIB-nanomanipulators," *Journal of Physics: Conference Series*, vol. 126, p. 012031, Aug. 2008.
- [121] H. Wu, H.-Y. Cha, M. Chandrashekhar, M. G. Spencer, and G. Koley, "High-yield GaN nanowire synthesis and field-effect transistor fabrication," *Journal of Electronic Materials*, vol. 35, pp. 670–674, Apr. 2006.
- [122] K. A. Dick, J. Bolinsson, B. M. Borg, and J. Johansson, "Controlling the Abruptness of Axial Heterojunctions in III–V Nanowires: Beyond the Reservoir Effect," *Nano Letters*, vol. 12, pp. 3200–3206, June 2012.
- [123] E. W. Müller, "Field ion microscopy," tech. rep., PENNSYLVANIA STATE UNIV STATE COLLEGE FIELD EMISSION LAB, 1969.
- [124] F. Danoix and F. Vurpillot, "Chapter Three - Basics of Field Ion Microscopy," in *Atom Probe Tomography* (W. Lefebvre-Ulrikson, F. Vurpillot, and X. Sauvage, eds.), pp. 73–95, Academic Press, Jan. 2016.
- [125] C. G. Sánchez *, A. Y. Iozovoi, and A. Alavi, "Field-evaporation from first-principles," *Molecular Physics*, vol. 102, pp. 1045–1055, May 2004.
- [126] M. K. Miller, *Atom Probe Tomography: Analysis at the Atomic Level*. Springer Science & Business Media, Dec. 2012.
- [127] M. K. Miller and R. G. Forbes, *Atom-Probe Tomography*. Boston, MA: Springer US, 2014.
- [128] D. Saxey, D. Moser, S. Piazzolo, S. Reddy, and J. Valley, "Atomic worlds: Current state and future of atom probe tomography in geoscience," *Scripta Materialia*, vol. 148, pp. 115–121, Apr. 2018.
- [129] A. Vella, "On the interaction of an ultra-fast laser with a nanometric tip by laser assisted atom probe tomography: A review," *Ultramicroscopy*, vol. 132, pp. 5–18, Sept. 2013.
- [130] E. D. Russo, I. Blum, J. Houard, G. D. Costa, D. Blavette, and L. Rigutti, "Field-Dependent Measurement of GaAs Composition by Atom Probe Tomography," *Microscopy and Microanalysis*, vol. 23, pp. 1067–1075, Dec. 2017.
- [131] T. Hashizume, Y. Hasegawa, A. Kobayashi, and T. Sakurai, "Atom-probe investigation of III–V semiconductors: Comparison of voltage-pulse and laser-pulse modes," *Review of Scientific Instruments*, vol. 57, pp. 1378–1380, July 1986.

- [132] N. Jeon, *Composition Modulations Driven by Surface Faceting of GaAs-AlGaAs Core-Shell Nanowires*. PhD thesis, Northwestern University, Evanston IL, 2016.
- [133] F. Vurpillot, A. Bostel, and D. Blavette, "Trajectory overlaps and local magnification in three-dimensional atom probe," *Applied Physics Letters*, vol. 76, pp. 3127–3129, May 2000.
- [134] N. Jeon and L. J. Lauhon, "Chapter Six - Atom Probe Tomography of Nanowires," in *Semiconductors and Semimetals* (A. F. I. Morral, S. A. Dayeh, and C. Jagadish, eds.), vol. 93 of *Semiconductor Nanowires I*, pp. 249–278, Elsevier, Jan. 2015.
- [135] M. I. Nave, "Materials Science of Electrochemical Formation of Tungsten Nanosharp Probes," p. 237.
- [136] Y. Zhang, *Three dimensional atom probe tomography of nanoscale thin films, interfaces and particles*. Doctor of Philosophy, Iowa State University, Digital Repository, Ames, 2009.
- [137] A. Devaraj, D. E. Perea, J. Liu, L. M. Gordon, T. J. Prosa, P. Parikh, D. R. Diercks, S. Meher, R. P. Kolli, Y. S. Meng, and S. Thevuthasan, "Three-dimensional nanoscale characterisation of materials by atom probe tomography," *International Materials Reviews*, vol. 63, pp. 68–101, Feb. 2018.
- [138] M. K. Miller, K. F. Russell, K. Thompson, R. Alvis, and D. J. Larson, "Review of Atom Probe FIB-Based Specimen Preparation Methods," *Microscopy and Microanalysis*, vol. 13, pp. 428–436, Dec. 2007.
- [139] H. Blumtritt, D. Isheim, S. Senz, D. N. Seidman, and O. Moutanabbir, "Preparation of nanowire specimens for laser-assisted atom probe tomography," *Nanotechnology*, vol. 25, p. 435704, Oct. 2014.
- [140] Z. Sun, O. Hazut, B.-C. Huang, Y.-P. Chiu, C.-S. Chang, R. Yerushalmi, L. J. Lauhon, and D. N. Seidman, "Dopant Diffusion and Activation in Silicon Nanowires Fabricated by ex Situ Doping: A Correlative Study via Atom-Probe Tomography and Scanning Tunneling Spectroscopy," *Nano Letters*, vol. 16, pp. 4490–4500, July 2016.
- [141] D. E. Newbury and N. W. M. Ritchie, "Is Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometry (SEM/EDS) Quantitative?," *Scanning*, vol. 35, no. 3, pp. 141–168, 2013.
- [142] A. J. Schwartz, M. Kumar, B. L. Adams, and D. P. Field, eds., *Electron Backscatter Diffraction in Materials Science*. Boston, MA: Springer US, 2009.
- [143] W. Xu, M. Ferry, N. Mateescu, J. M. Cairney, and F. J. Humphreys, "Techniques for generating 3-D EBSD microstructures by FIB tomography," *Materials Characterization*, vol. 58, pp. 961–967, Oct. 2007.
- [144] J. Guyon, N. Gey, D. Goran, S. Chalal, and F. Pérez-Willard, "Advancing FIB assisted 3D EBSD using a static sample setup," *Ultramicroscopy*, vol. 161, pp. 161–167, Feb. 2016.
- [145] L. Reimer, *Transmission Electron Microscopy: Physics of Image Formation and Microanalysis*. Springer, Nov. 2013.
- [146] C. Hetherington, "Aberration correction for TEM," *Materials Today*, vol. 7, pp. 50–55, Dec. 2004.
- [147] P. Buseck, J. Cowley, and L. Eyring, *High-Resolution Transmission Electron Microscopy: and Associated Techniques*. Oxford University Press, Feb. 1989.
- [148] P. D. Brown, "Transmission Electron Microscopy-A Textbook for Materials Science, by David B. Williams and C. Barry Carter," *Microscopy and Microanalysis*, vol. 5, no. 6, pp. 452–453, 1999.
- [149] D. Cooper, T. Denneulin, N. Bernier, A. Béch  , and J.-L. Rouvi  re, "Strain mapping of semiconductor specimens with nm-scale resolution in a transmission electron microscope," *Micron*, vol. 80, pp. 145–165, Jan. 2016.
- [150] M. J. H  ych and L. Potez, "Geometric phase analysis of high-resolution electron microscopy images of antiphase domains: Example Cu₃Au," *Philosophical Magazine A*, vol. 76, pp. 1119–1138, Dec. 1997.
- [151] J. M. Zuo and J. C. H. Spence, "Strain Measurements and Mapping," in *Advanced Transmission Electron Microscopy: Imaging and Diffraction in Nanoscience* (J. M. Zuo and J. C. Spence, eds.), pp. 553–580, New York, NY: Springer, 2017.

- [152] M. Scimeca, S. Bischetti, H. K. Lamsira, R. Bonfiglio, and E. Bonanno, "Energy Dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis," *European Journal of Histochemistry : EJH*, vol. 62, Mar. 2018.
- [153] L. J. Allen, A. J. D'Alfonso, B. Freitag, and D. O. Klenov, "Chemical mapping at atomic resolution using energy-dispersive x-ray spectroscopy," *MRS bulletin*, vol. 37, no. 1, pp. 47–52, 2012.
- [154] H. MÜllejans and J. Bruley, "Electron energy-loss spectroscopy (EELS) ; comparison with X-ray analysis," *Journal de Physique IV Colloque*, vol. 03, no. C7, pp. C7–2083–C7–2092, 1993.
- [155] D. Nunes, A. Pimentel, M. Matias, T. Freire, A. Araújo, F. Silva, P. Gaspar, S. Garcia, P. A. Carvalho, and E. Fortunato, "Tailoring upconversion and morphology of Yb/Eu doped Y2O3 nanostructures by acid composition mediation," *Nanomaterials*, vol. 9, no. 2, p. 234, 2019.
- [156] P. A. Midgley and R. E. Dunin-Borkowski, "Electron tomography and holography in materials science," *Nature Materials*, vol. 8, pp. 271–280, Apr. 2009.
- [157] K. Lepinay, F. Lorut, R. Pantel, and T. Epicier, "Chemical 3D tomography of 28nm high K metal gate transistor: STEM XEDS experimental method and results," *Micron*, vol. 47, pp. 43–49, Apr. 2013.
- [158] K. Jarausch, P. Thomas, D. N. Leonard, R. Twesten, and C. R. Booth, "Four-dimensional STEM-EELS: Enabling nano-scale chemical tomography," *Ultramicroscopy*, vol. 109, pp. 326–337, Mar. 2009.
- [159] R. Pantel and G. Servanton, "Dopant Distribution Quantitative Analysis Using STEM-EELS/EDX Spectroscopy Techniques," in *Transmission Electron Microscopy in Micro-Nanoelectronics*, pp. 37–64, John Wiley & Sons, Ltd, 2013.
- [160] G. Servanton, R. Pantel, M. Juhel, and F. Bertin, "STEM EDX applications for arsenic dopant mapping in nanometer scale silicon devices," *Journal of Physics: Conference Series*, vol. 209, p. 012044, Feb. 2010.
- [161] B. Goris, M. Meledina, S. Turner, Z. Zhong, K. J. Batenburg, and S. Bals, "Three dimensional mapping of Fe dopants in ceria nanocrystals using direct spectroscopic electron tomography," *Ultramicroscopy*, vol. 171, pp. 55–62, Dec. 2016.
- [162] S. Gao, P. Wang, F. Zhang, G. T. Martinez, P. D. Nellist, X. Pan, and A. I. Kirkland, "Electron ptychographic microscopy for three-dimensional imaging," *Nature Communications*, vol. 8, pp. 1–8, July 2017.
- [163] B. Goris, J. De Beenhouwer, A. De Backer, D. Zanaga, K. J. Batenburg, A. Sánchez-Iglesias, L. M. Liz-Marzán, S. Van Aert, S. Bals, J. Sijbers, and G. Van Tendeloo, "Measuring Lattice Strain in Three Dimensions through Electron Microscopy," *Nano Letters*, vol. 15, pp. 6996–7001, Oct. 2015.
- [164] R. Xu, C.-C. Chen, L. Wu, M. C. Scott, W. Theis, C. Ophus, M. Bartels, Y. Yang, H. Ramezani-Dakhel, M. R. Sawaya, H. Heinz, L. D. Marks, P. Ercius, and J. Miao, "Three-dimensional coordinates of individual atoms in materials revealed by electron tomography," *Nature Materials*, vol. 14, pp. 1099–1103, Nov. 2015.
- [165] K. Friedrich, "LAUE," X-Ray Diffraction Phenomenon," *Ber. Bayer. Akad. Wiss*, pp. 303–322, 1912.
- [166] M. Eckert, "Max von Laue and the discovery of X-ray diffraction in 1912," *Annalen der Physik*, vol. 524, no. 5, pp. A83–A85, 2012.
- [167] W. L. Bragg, "The Specular Reflection of X-rays.," *Nature*, vol. 90, pp. 410–410, Dec. 1912.
- [168] W. H. Bragg and W. L. Bragg, "The reflection of X-rays by crystals," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol. 88, pp. 428–438, July 1913.
- [169] C. Hammond and C. Hammond, *The basics of cristallography and diffraction*, vol. 214. Oxford, 2001.

- [170] K. Hermann, “Basics of Crystallography,” in *Computational Methods in Catalysis and Materials Science*, pp. 265–294, John Wiley & Sons, Ltd, 2009.
- [171] P. Scherrer, “Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels Röntgenstrahlen,” in *Kolloidchemie Ein Lehrbuch* (R. Zsigmondy, ed.), Chemische Technologie in Einzeldarstellungen, pp. 387–409, Berlin, Heidelberg: Springer, 1912.
- [172] J. B. Cohen, “Diffraction methods in materials science,” 1966, 357 P. *The MacMillan Co., New York*, 1966.
- [173] W. Borchardt-Ott, ed., *Crystallography*. Berlin Heidelberg: Springer-Verlag, 2 ed., 1995.
- [174] J. Stangl, C. Mocuta, V. Chamard, and D. Carbone, *Nanobeam X-Ray Scattering: Probing Matter at the Nanoscale*. John Wiley & Sons, Sept. 2013.
- [175] C. Suryanarayana and M. G. Norton, *X-Ray Diffraction*. Boston, MA: Springer US, 1998.
- [176] B. Gil, *Physics of Wurtzite Nitrides and Oxides*, vol. 197 of *Springer Series in Materials Science*. Cham: Springer International Publishing, 2014.
- [177] M. De Graef and M. E. McHenry, *Structure of materials: an introduction to crystallography, diffraction and symmetry*. Cambridge University Press, 2012.
- [178] G. Taylor, “The phase problem,” *Acta Crystallographica Section D: Biological Crystallography*, vol. 59, pp. 1881–1890, Nov. 2003.
- [179] J. M. J. Madey, “Stimulated Emission of Bremsstrahlung in a Periodic Magnetic Field,” *Journal of Applied Physics*, vol. 42, pp. 1906–1913, Apr. 1971.
- [180] Z. Huang and K.-J. Kim, “Review of x-ray free-electron laser theory,” *Physical Review Special Topics - Accelerators and Beams*, vol. 10, Mar. 2007.
- [181] B. W. J. McNeil and N. R. Thompson, “X-ray free-electron lasers,” *Nature Photonics*, vol. 4, pp. 814–821, Dec. 2010.
- [182] A. Novokhatski, “Coherent synchrotron radiation: theory and simulations,” p. 15.
- [183] M. Eriksson, J. F. v. d. Veen, and C. Quitmann, “Diffraction-limited storage rings – a window to the science of tomorrow,” *Journal of Synchrotron Radiation*, vol. 21, pp. 837–842, Sept. 2014.
- [184] G. Margaritondo, Y. Hwu, and G. Tromba, “Synchrotron light: From basics to coherence and coherence-related applications,” p. 29.
- [185] M. D. Schroer and J. R. Petta, “Correlating the nanostructure and electronic properties of InAs nanowires,” *Nano Lett.*, vol. 10, no. 5, pp. 1618–1622. DOI: 10.1021/nl904053j, 2010.
- [186] J. H. Hubbell and S. M. Seltzer, “NIST Standard Reference Database 126: X-ray Mass Attenuation Coefficients,” July 2004.
- [187] B. L. Henke, E. M. Gullikson, and J. Davis, “CXRO X-Ray Interactions With Matter,” July 1993.
- [188] A. Snigirev, V. Kohn, I. Snigireva, and B. Lengeler, “A compound refractive lens for focusing high-energy X-rays,” *Nature*, vol. 384, pp. 49–51, Nov. 1996.
- [189] G. E. Ice, J.-S. Chung, J. Z. Tischler, A. Lunt, and L. Assoufid, “Elliptical x-ray microprobe mirrors by differential deposition,” *Review of Scientific Instruments*, vol. 71, pp. 2635–2639, June 2000.
- [190] N. Kujala, S. Marathe, D. Shu, B. Shi, J. Qian, E. Maxey, L. Finney, A. Macrander, and L. Assoufid, “Kirkpatrick-Baez mirrors to focus hard X-rays in two dimensions as fabricated, tested and installed at the Advanced Photon Source,” *Journal of Synchrotron Radiation*, vol. 21, pp. 662–668, July 2014.
- [191] G. E. Ice, “Microbeam-forming methods for synchrotron radiation,” *X-Ray Spectrometry*, vol. 26, no. 6, pp. 315–326, 1997.
- [192] C. G. Schroer and B. Lengeler, “X-Ray Optics,” in *Springer Handbook of Lasers and Optics* (F. Träger, ed.), Springer Handbooks, pp. 1461–1474, Berlin, Heidelberg: Springer, 2012.
- [193] A. Thompson, D. Attwood, E. Gullikson, M. Howells, K.-J. Kim, J. Kirz, J. Kortright, I. Lindau, Y. Liu, P. Pianetta, A. Robinson, J. Scofield, J. Underwood, G. Williams, and H. Winick, *X-Ray Data Booklet*. Center for X-ray Optics and Advanced Light Source, Oct. 2009.

- [194] H. Yan, H. C. Kang, R. Conley, C. Liu, A. T. Macrander, G. B. Stephenson, and J. Maser, "Multilayer Laue Lens: A Path Toward One Nanometer X-Ray Focusing," 2010.
- [195] I. Mohacsi, I. Vartiainen, B. Rösner, M. Guizar-Sicairos, V. A. Guzenko, I. McNulty, R. Winarski, M. V. Holt, and C. David, "Interlaced zone plate optics for hard X-ray imaging in the 10 nm range," *Scientific Reports*, vol. 7, pp. 1–10, Mar. 2017.
- [196] S. Bajt, M. Prasciolu, H. Fleckenstein, M. Domaracký, H. N. Chapman, A. J. Morgan, O. Yefanov, M. Messerschmidt, Y. Du, K. T. Murray, V. Mariani, M. Kuhn, S. Aplin, K. Pande, P. Villanueva-Perez, K. Stachnik, J. P. Chen, A. Andrejczuk, A. Meents, A. Burkhardt, D. Pennicard, X. Huang, H. Yan, E. Nazaretski, Y. S. Chu, and C. E. Hamm, "X-ray focusing with efficient high-NA multilayer Laue lenses," *Light: Science & Applications*, vol. 7, pp. 17162–17162, Mar. 2018.
- [197] I. Robinson, C. Kenney-Benson, and I. Vartanyants, "Sources of decoherence in beamline optics," *Physica B: Condensed Matter*, vol. 336, pp. 56–62, Aug. 2003.
- [198] J. Als-Nielsen, *Elements of modern X-ray physics*. New York, 2001.
- [199] Y. Sekiguchi, T. Oroguchi, and M. Nakasako, "Classification and assessment of retrieved electron density maps in coherent X-ray diffraction imaging using multivariate analysis," *Journal of Synchrotron Radiation*, vol. 23, pp. 312–323, Jan. 2016.
- [200] J. Miao, T. Ishikawa, I. K. Robinson, and M. M. Murnane, "Beyond crystallography: Diffractive imaging using coherent x-ray light sources," *Science*, vol. 348, pp. 530–535, May 2015.
- [201] G. Xiong, O. Moutanabbir, M. Reiche, R. Harder, and I. Robinson, "Coherent X-Ray Diffraction Imaging and Characterization of Strain in Silicon-on-Insulator Nanostructures," *Advanced Materials*, vol. 26, no. 46, pp. 7747–7763, 2014.
- [202] J. R. Fienup, "Phase retrieval algorithms: a comparison," *Applied optics*, vol. 21, no. 15, pp. 2758–2769, 1982.
- [203] J. R. Fienup, "Phase retrieval algorithms: a personal tour [Invited]," *Applied Optics*, vol. 52, pp. 45–56, Jan. 2013.
- [204] R. W. Gerchberg, "A practical algorithm for the determination of phase from image and diffraction plane pictures," *Optik*, vol. 35, pp. 237–246, 1972.
- [205] J. Miao, J. Kirz, and D. Sayre, "The oversampling phasing method," *Acta Crystallographica Section D: Biological Crystallography*, vol. 56, pp. 1312–1315, Oct. 2000.
- [206] W. Cha, A. Ulvestad, M. Allain, V. Chamard, R. Harder, S. J. Leake, J. Maser, P. H. Fuoss, and S. O. Hruszkewycz, "Three Dimensional Variable-Wavelength X-Ray Bragg Coherent Diffraction Imaging," *Physical Review Letters*, vol. 117, p. 225501, Nov. 2016.
- [207] D. Dzhigaev, T. Stankevič, I. Besedin, S. Lazarev, A. Shabalin, M. N. Strikhanov, R. Feidenhans'l, and I. A. Vartanyants, "Theoretical analysis of the strain mapping in a single core-shell nanowire by x-ray Bragg ptychography," in *X-Ray Nanoimaging: Instruments and Methods II*, vol. 9592, p. 95920S, International Society for Optics and Photonics, Sept. 2015.
- [208] M. A. Pfeifer, G. J. Williams, I. A. Vartanyants, R. Harder, and I. K. Robinson, "Three-dimensional mapping of a deformation field inside a nanocrystal," *Nature*, vol. 442, pp. 63–66, July 2006.
- [209] I. Robinson and R. Harder, "Coherent X-ray diffraction imaging of strain at the nanoscale," *Nature Materials*, vol. 8, pp. 291–298, Apr. 2009.
- [210] W. Cha, Y. Liu, H. You, G. B. Stephenson, and A. Ulvestad, "Dealloying in Individual Nanoparticles and Thin Film Grains: A Bragg Coherent Diffractive Imaging Study," *Advanced Functional Materials*, vol. 27, no. 25, p. 1700331, 2017.
- [211] A. Yau, W. Cha, M. W. Kanan, G. B. Stephenson, and A. Ulvestad, "Bragg coherent diffractive imaging of single-grain defect dynamics in polycrystalline films," *Science*, vol. 356, pp. 739–742, May 2017.
- [212] N. Vaxelaire, H. Proudhon, S. Labat, C. Kirchlechner, J. Keckes, V. Jacques, S. Ravy, S. Forest, and O. Thomas, "Methodology for studying strain inhomogeneities in polycrystalline thin films duringin

- sitothermal loading using coherent x-ray diffraction,” *New Journal of Physics*, vol. 12, p. 035018, Mar. 2010.
- [213] X. Shi, J. N. Clark, G. Xiong, X. Huang, R. Harder, and I. K. Robinson, “Mechanical breakdown of bent silicon nanowires imaged by coherent x-ray diffraction,” *New Journal of Physics*, vol. 15, p. 123007, Dec. 2013.
 - [214] A. Ulvestad, J. N. Clark, R. Harder, I. K. Robinson, and O. G. Shpyrko, “3D imaging of twin domain defects in gold nanoparticles,” *Nano Lett.*, vol. 15, pp. 4066–4070, DOI: 10.1021/acs.nanolett.5b01104, June 2015.
 - [215] Y. Liu, P. P. Lopes, W. Cha, R. Harder, J. Maser, E. Maxey, M. J. Highland, N. M. Markovic, S. O. Hruszkewycz, and G. B. Stephenson, “Stability limits and defect dynamics in Ag nanoparticles probed by bragg coherent diffractive imaging,” *Nano letters*, vol. 17, no. 3, pp. 1595–1601, 2017.
 - [216] A. Ulvestad, M. Menickelly, and S. M. Wild, “Accurate, rapid identification of dislocation lines in coherent diffractive imaging via a min-max optimization formulation,” *AIP Advances*, vol. 8, no. 1, p. 015114, 2018.
 - [217] S. T. Haag, M.-I. Richard, S. Labat, M. Gailhanou, U. Welzel, E. J. Mittemeijer, and O. Thomas, “Anomalous coherent diffraction of core-shell nano-objects: A methodology for determination of composition and strain fields,” *Physical Review B*, vol. 87, p. 035408, Jan. 2013.
 - [218] A. Diaz, C. Mocuta, J. Stangl, B. Mandl, C. David, J. Vila-Comamala, V. Chamard, T. H. Metzger, and G. Bauer, “Coherent diffraction imaging of a single epitaxial InAs nanowire using a focused x-ray beam,” *Physical Review B*, vol. 79, p. 125324, Mar. 2009. Publisher: American Physical Society.
 - [219] V. Favre-Nicolin, J. Eymery, R. Koester, and P. Gentile, “Coherent-diffraction imaging of single nanowires of diameter 95 nanometers,” *Physical Review B*, vol. 79, p. 195401, May 2009.
 - [220] V. Favre-Nicolin, F. Mastropietro, J. Eymery, D. Camacho, Y. M. Niquet, B. M. Borg, M. E. Messing, L.-E. Wernersson, R. E. Algra, and E. Bakkers, “Analysis of strain and stacking faults in single nanowires using Bragg coherent diffraction imaging,” *New Journal of Physics*, vol. 12, no. 3, p. 035013, 2010. ISBN: 1367-2630 Publisher: IOP Publishing.
 - [221] M. C. Newton, M. Sao, Y. Fujisawa, R. Onitsuka, T. Kawaguchi, K. Tokuda, T. Sato, T. Togashi, M. Yabashi, T. Ishikawa, T. Ichitsubo, E. Matsubara, Y. Tanaka, and Y. Nishino, “Time-Resolved Coherent Diffraction of Ultrafast Structural Dynamics in a Single Nanowire,” *Nano Letters*, vol. 14, pp. 2413–2418, May 2014.
 - [222] S. T. Haag, M.-I. Richard, U. Welzel, V. Favre-Nicolin, O. Balmes, G. Richter, E. J. Mittemeijer, and O. Thomas, “Concentration and Strain Fields inside a Ag/Au Core-Shell Nanowire Studied by Coherent X-ray Diffraction,” *Nano Letters*, vol. 13, pp. 1883–1889, May 2013.
 - [223] A. Davtyan, V. Favre-Nicolin, R. B. Lewis, H. Küpers, L. Geelhaar, D. Kriegner, D. Bahrami, A. Al-Hassan, G. Chahine, O. Loffeld, and U. Pietsch, “Coherent X-ray diffraction imaging meets ptychography to study core-shell-shell nanowires,” *MRS Advances*, vol. 3, no. 39, pp. 2317–2322, 2018.
 - [224] X. Huang, R. Harder, S. Leake, J. Clark, and I. Robinson, “Three-dimensional Bragg coherent diffraction imaging of an extended ZnO crystal,” *Journal of Applied Crystallography*, vol. 45, pp. 778–784, Aug. 2012.
 - [225] A. Davtyan, A. Biermanns, O. Loffeld, and U. Pietsch, “Determination of the stacking fault density in highly defective single GaAs nanowires by means of coherent diffraction imaging,” *New Journal of Physics*, vol. 18, no. 6, p. 063021, 2016.
 - [226] V. Chamard, J. Stangl, S. Labat, B. Mandl, R. T. Lechner, and T. H. Metzger, “Evidence of stacking-fault distribution along an InAs nanowire using micro-focused coherent X-ray diffraction,” *Journal of Applied Crystallography*, vol. 41, pp. 272–280, Apr. 2008.

- [227] V. Chamard, A. Diaz, J. Stangl, and S. Labat, "Structural investigation of InAs nanowires with coherent X-rays," *The Journal of Strain Analysis for Engineering Design*, vol. 44, pp. 533–542, Oct. 2009.
- [228] J. Shin, T. W. Cornelius, S. Labat, F. Lauraux, M.-I. Richard, G. Richter, N. P. Blanchard, D. S. Gianola, and O. Thomas, "In situ Bragg coherent X-ray diffraction during tensile testing of an individual Au nanowire," *Journal of Applied Crystallography*, vol. 51, pp. 781–788, June 2018.
- [229] J. Gulden, S. O. Mariager, A. P. Mancuso, O. M. Yefanov, J. Baltser, P. Krogstrup, J. Patommel, M. Burghammer, R. Feidenhans'l, and I. A. Vartanyants, "Coherent X-ray nanodiffraction on single GaAs nanowires," *physica status solidi (a)*, vol. 208, no. 11, pp. 2495–2498, 2011.
- [230] A. Davydok, T. W. Cornelius, Z. Ren, C. Leclerc, G. Chahine, T. Schüllli, F. Lauraux, G. Richter, and O. Thomas, "In Situ Coherent X-ray Diffraction during Three-Point Bending of a Au Nanowire: Visualization and Quantification," *Quantum Beam Science*, vol. 2, p. 24, Dec. 2018.
- [231] J. Hagemann, A.-L. Robisch, M. Osterhoff, and T. Salditt, "Probe reconstruction for holographic X-ray imaging," *Journal of Synchrotron Radiation*, vol. 24, pp. 498–505, Mar. 2017.
- [232] F. Hüe, J. M. Rodenburg, A. M. Maiden, F. Sweeney, and P. A. Midgley, "Wave-front phase retrieval in transmission electron microscopy via ptychography," *Physical Review B*, vol. 82, p. 121415, Sept. 2010.
- [233] T. B. Edo, D. J. Batey, A. M. Maiden, C. Rau, U. Wagner, Z. D. Pešić, T. A. Waigh, and J. M. Rodenburg, "Sampling in x-ray ptychography," *Physical Review A*, vol. 87, May 2013.
- [234] C. Yang, J. Qian, A. Schirotzek, F. Maia, and S. Marchesini, "Iterative Algorithms for Ptychographic Phase Retrieval," May 2011.
- [235] A. Maiden, D. Johnson, and P. Li, "Further improvements to the ptychographical iterative engine," *Optica*, vol. 4, pp. 736–745, July 2017.
- [236] S. O. Hruszkewycz, M. V. Holt, A. Tripathi, J. Maser, and P. H. Fuoss, "Framework for three-dimensional coherent diffraction imaging by focused beam x-ray Bragg ptychography," *Optics Letters*, vol. 36, pp. 2227–2229, June 2011.
- [237] P. Godard, G. Carbone, M. Allain, F. Mastropietro, G. Chen, L. Capello, A. Diaz, T. H. Metzger, J. Stangl, and V. Chamard, "Three-dimensional high-resolution quantitative microscopy of extended crystals," *Nature Communications*, vol. 2, pp. 1–6, Nov. 2011.
- [238] X. Huang, K. Lauer, J. N. Clark, W. Xu, E. Nazaretski, R. Harder, I. K. Robinson, and Y. S. Chu, "Fly-scan ptychography," *Scientific Reports*, vol. 5, pp. 1–5, Mar. 2015.
- [239] P. Godard, M. Allain, and V. Chamard, "Imaging of highly inhomogeneous strain field in nanocrystals using x-ray Bragg ptychography: A numerical study," *Phys. Rev. B*, vol. 84, no. 14, p. 144109. DOI: 10.1103/PhysRevB.84.144109, 2011.
- [240] D. Dzhigaev, T. Stankevič, Z. Bi, S. Lazarev, M. Rose, A. Shabalin, J. Reinhardt, A. Mikkelsen, L. Samuelson, and G. Falkenberg, "X-ray bragg ptychography on a single InGaN/GaN core-shell nanowire," *ACS Nano*, vol. 11, pp. 6605–6611. DOI: 10.1021/acsnano.6b08122, 2017. tex.publisher: ACS Publications.
- [241] S. O. Hruszkewycz, M. V. Holt, C. E. Murray, J. Bruley, J. Holt, A. Tripathi, O. G. Shpyrko, I. McNulty, M. J. Highland, and P. H. Fuoss, "Quantitative nanoscale imaging of lattice distortions in epitaxial semiconductor heterostructures using nanofocused x-ray bragg projection ptychography," *Nano Lett.*, vol. 12, pp. 5148–5154. DOI: 10.1021/nl303201w, Oct. 2012.
- [242] S. O. Hruszkewycz, M. Allain, M. V. Holt, C. E. Murray, J. R. Holt, P. H. Fuoss, and V. Chamard, "High-resolution three-dimensional structural microscopy by single-angle Bragg ptychography," *Nat. Mater.*, vol. 16, pp. 244–251. DOI: 10.1038/nmat4798, Nov. 2016.
- [243] I. Calvo-Almazán, A. P. Ulvestad, E. Colegrove, T. Ablekim, M. V. Holt, M. O. Hill, S. Maddali, L. J. Lauhon, M. I. Bertoni, X. Huang, H. Yan, E. Nazaretski, Y. S. Chu, S. O. Hruszkewycz, and M. E. Stuckelberger, "Strain Mapping of CdTe Grains in Photovoltaic Devices," *IEEE Journal of*

- Photovoltaics*, vol. 9, pp. 1790–1799, Nov. 2019. Conference Name: IEEE Journal of Photovoltaics.
- [244] T. Stankevič, E. Hilner, F. Seiboth, R. Ciechonski, G. Vescovi, O. Kryliouk, U. Johansson, L. Samuelson, G. Wellenreuther, and G. Falkenberg, “Fast strain mapping of nanowire light-emitting diodes using nanofocused x-ray beams,” *ACS Nano*, vol. 9, no. 7, pp. 6978–6984. DOI: 10.1021/acsnano.5b01291, 2015. tex.publisher: ACS Publications.
 - [245] J. Wallentin, D. Jacobsson, M. Osterhoff, M. T. Borgström, and T. Salditt, “Bending and twisted lattice tilt in strained core-shell nanowires revealed by nanofocused X-ray diffraction,” *Nano Lett.*, vol. 17, no. 7, pp. 4143–4150. DOI: 10.1021/acs.nanolett.7b00918, 2017.
 - [246] T. Stankevič, D. Dzhigaev, Z. Bi, M. Rose, A. Shabalin, J. Reinhardt, A. Mikkelsen, L. Samuelson, G. Falkenberg, and I. A. Vartanyants, “Nanofocused x-ray beams applied for mapping strain in core-shell nanowires,” in *X-Ray Nanoimaging: Instruments and Methods II*, vol. 9592, p. 95920D, International Society for Optics and Photonics, 2015.
 - [247] K. Röhl, “Analysis of stress and strain distribution in thin films and substrates,” *Journal of Applied Physics*, vol. 47, pp. 3224–3229, July 1976.
 - [248] E. M. Santos and D. Faurie, “Elastic constants and stress-strain in thin films: application in fiber-textured gold film by X-Ray diffraction,” *arXiv:1804.01570 [cond-mat]*, Apr. 2018.
 - [249] Y. He, Y. Zhao, C. Fan, X. Liu, and R. Han, “Simulation of inhomogeneous strain in Ge-Si core-shell nanowires,” *Frontiers of Electrical and Electronic Engineering in China*, vol. 4, pp. 342–347, Sept. 2009.
 - [250] T. E. Trammell, X. Zhang, Y. Li, L.-Q. Chen, and E. C. Dickey, “Equilibrium strain-energy analysis of coherently strained core-shell nanowires,” *Journal of Crystal Growth*, vol. 310, pp. 3084–3092, June 2008.
 - [251] J. Grönqvist, N. Søndergaard, F. Boxberg, T. Guhr, S. Åberg, and H. Q. Xu, “Strain in semiconductor core-shell nanowires,” *Journal of Applied Physics*, vol. 106, p. 053508, Sept. 2009.
 - [252] C. O. Horgan, “Saint-Venant End Effects In Composites,” *Journal of Composite Materials*, vol. 16, pp. 411–422, Sept. 1982.
 - [253] C. A. Klein and R. P. Miller, “Strains and stresses in multilayered elastic structures: The case of chemically vapor-deposited ZnS/ZnSe laminates,” *Journal of Applied Physics*, vol. 87, pp. 2265–2272, Mar. 2000.
 - [254] N. Sköld, L. S. Karlsson, M. W. Larsson, M.-E. Pistol, W. Seifert, J. Trägårdh, and L. Samuelson, “Growth and Optical Properties of Strained GaAs-GaxIn_{1-x}P Core-Shell Nanowires,” *Nano Letters*, vol. 5, pp. 1943–1947, Oct. 2005.
 - [255] H. X. Zhu, “The effects of surface and initial stresses on the bending stiffness of nanowires,” *Nanotechnology*, vol. 19, p. 405703, Aug. 2008.
 - [256] R. Singh, E. J. Dailey, J. Drucker, and J. Menéndez, “Raman scattering from Ge-Si core-shell nanowires: Validity of analytical strain models,” *Journal of Applied Physics*, vol. 110, p. 124305, Dec. 2011.
 - [257] D. Ferrand and J. Cibert, “Strain in crystalline core-shell nanowires,” *The European Physical Journal-Applied Physics*, vol. 67, no. 3, 2014.
 - [258] D. Kriegner, C. Panse, B. Mandl, K. A. Dick, M. Keplinger, J. M. Persson, P. Caroff, D. Ercolani, L. Sorba, and F. Bechstedt, “Unit cell structure of crystal polytypes in InAs and InSb nanowires,” *Nano letters*, vol. 11, no. 4, pp. 1483–1489, 2011.
 - [259] D. Jacobsson, *Crystal Structures in GaAs Nanowires - Growth and Characterization*. PhD thesis, Lund University, Lund, 2015.
 - [260] L. Xing-Xiu, T. Xiao-Ma, C. Hong-Mei, O. Yi-Fang, and D. Yong, “The pressure dependences of elastic and lattice dynamic properties of AlAs from ab initio calculations,” *Chinese Physics B*, vol. 22, no. 2, p. 026201, 2013.

- [261] S. D. Dabhi and P. K. Jha, "Phonon dispersion and Raman spectra of wurtzite InAs under pressure," *Journal of Physics and Chemistry of Solids*, vol. 83, pp. 70–74, 2015.
- [262] O. Salehzadeh, K. L. Kavanagh, and S. P. Watkins, "Geometric limits of coherent III-V core/shell nanowires," *Journal of Applied Physics*, vol. 114, p. 054301, Aug. 2013.
- [263] K. Ho-Le, "Finite element mesh generation methods: a review and classification," *Computer-Aided Design*, vol. 20, pp. 27–38, Jan. 1988.
- [264] T. Pin and T. H. H. Pian, "The convergence of finite element method in solving linear elastic problems," *International Journal of Solids and Structures*, vol. 3, pp. 865–879, Sept. 1967.
- [265] S.-H. Park, D. Ahn, and Y.-T. Lee, "Finite element analysis of valence band structures in quantum wires," *Journal of Applied Physics*, vol. 96, pp. 2055–2062, Aug. 2004.
- [266] Z. Zanolli, L. E. Fröberg, M. T. Björk, M. E. Pistol, and L. Samuelson, "Fabrication, optical characterization and modeling of strained core-shell nanowires," *Thin Solid Films*, vol. 515, pp. 793–796, Oct. 2006.
- [267] S. Q. Wang and H. Q. Ye, "First-principles study on elastic properties and phase stability of III-V compounds," *physica status solidi (b)*, vol. 240, pp. 45–54, Nov. 2003.
- [268] Q. Zhang, P. W. Voorhees, and S. H. Davis, "Modeling of the growth of GaAs-AlGaAs core-shell nanowires," *Beilstein Journal of Nanotechnology*, vol. 8, pp. 506–513, Feb. 2017.
- [269] J. W. Matthews and A. E. Blakeslee, "Defects in epitaxial multilayers: I. Misfit dislocations," *Journal of Crystal Growth*, vol. 27, pp. 118–125, Dec. 1974.
- [270] T. Anan, K. Nishi, and S. Sugou, "Critical layer thickness on (111)B-oriented InGaAs/GaAs heteroepitaxy," *Applied Physics Letters*, vol. 60, pp. 3159–3161, June 1992.
- [271] T. Fleischmann, M. Moran, M. Hopkinson, H. Meidia, G. J. Rees, A. G. Cullis, J. L. Sánchez-Rojas, and I. Izpura, "Strained layer (111)B GaAs/InGaAs single quantum well lasers and the dependence of their characteristics upon indium composition," *Journal of Applied Physics*, vol. 89, pp. 4689–4696, May 2001.
- [272] S. Raychaudhuri and E. T. Yu, "Critical dimensions in coherently strained coaxial nanowire heterostructures," *Journal of Applied Physics*, vol. 99, p. 114308, June 2006.
- [273] S. Conesa-Boj, F. Boioli, E. Russo-Averchi, S. Dunand, M. Heiss, D. Rüffer, N. Wyrsh, C. Ballif, L. Miglio, and A. F. i. Morral, "Plastic and Elastic Strain Fields in GaAs/Si Core-Shell Nanowires," *Nano Letters*, vol. 14, pp. 1859–1864, Apr. 2014.
- [274] S. Wang, *Lattice engineering: technology and applications*. CRC Press, 2012.
- [275] F. Glas, "Strain in nanowires and nanowire heterostructures," in *Semiconductors and Semimetals*, vol. 93, pp. 79–123, Elsevier, 2015.
- [276] R. Popovitz-Biro, A. Kretinin, P. Von Huth, and H. Shtrikman, "InAs/GaAs Core-Shell Nanowires," *Crystal Growth & Design*, vol. 11, pp. 3858–3865, Sept. 2011.
- [277] S. O. Hruszkewycz, M. V. Holt, M. Allain, V. Chamard, S. M. Polvino, C. E. Murray, and P. H. Fuoss, "Efficient modeling of Bragg coherent x-ray nanobeam diffraction," *Optics Letters*, vol. 40, pp. 3241–3244, July 2015.
- [278] E. D. Hirlleman, "Modeling of multiple scattering effects in Fraunhofer diffraction particle size analysis," in *Optical Particle Sizing*, pp. 159–175, Springer, 1988.
- [279] P. Thibault, M. Dierolf, O. Bunk, A. Menzel, and F. Pfeiffer, "Probe retrieval in ptychographic coherent diffractive imaging," *Ultramicroscopy*, vol. 109, pp. 338–343, Mar. 2009.
- [280] A. N. Kurokhtin and A. V. Popov, "Simulation of high-resolution x-ray zone plates," *JOSA A*, vol. 19, pp. 315–324, Feb. 2002.
- [281] I. Mohacsi, P. Karvinen, I. Vartiainen, V. A. Guzenko, A. Somogyi, C. M. Kewish, P. Mercere, and C. David, "High-efficiency zone-plate optics for multi-keV X-ray focusing," *Journal of Synchrotron Radiation*, vol. 21, pp. 497–501, May 2014.

- [282] M. E. Brezinski, “7 - Noise and System Performance with TD-OCT and SD-OCT,” in *Optical Coherence Tomography* (M. E. Brezinski, ed.), pp. 175–195, Burlington: Academic Press, Jan. 2006.
- [283] A. F. Rigosi, “Analysis of Fraunhofer diffraction patterns’ entropy based on apertures shaped as national borders,” *Optik*, vol. 172, pp. 1019–1025, Nov. 2018.
- [284] G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics – Basic Principles and New Materials Developments*. 2001.
- [285] Z. Cui, R. Perumal, T. Ishikura, K. Konishi, K. Yoh, and J. Motohisa, “Characterizing the electron transport properties of a single <110> InAs nanowire,” *Applied Physics Express*, vol. 7, p. 085001, July 2014.
- [286] K. K. Smith, “Photoluminescence of semiconductor materials,” *Thin Solid Films*, vol. 84, pp. 171–182, Oct. 1981.
- [287] G. D. Gilliland, “Photoluminescence spectroscopy of crystalline semiconductors,” *Materials Science and Engineering: R: Reports*, vol. 18, pp. 99–399, Mar. 1997.
- [288] P. J. Dean, “Photoluminescence as a diagnostic of semiconductors,” *Progress in Crystal Growth and Characterization*, vol. 5, pp. 89–174, Jan. 1982.
- [289] S. J. Pennycook, L. M. Brown, and A. J. Craven, “Observation of cathodoluminescence at single dislocations by STEM,” *Philosophical Magazine A*, vol. 41, pp. 589–600, Apr. 1980.
- [290] A. Bouhelier, “Nanoscale Optical Imaging and Spectroscopy,” in *Reference Module in Materials Science and Materials Engineering*, Elsevier, Jan. 2016.
- [291] H. Selke, M. Amirsawadkouhi, P. L. Ryder, T. Böttcher, S. Einfeldt, D. Hommel, F. Bertram, and J. Christen, “Compositional inhomogeneities in InGaN studied by transmission electron microscopy and spatially resolved cathodoluminescence,” *Materials Science and Engineering: B*, vol. 59, pp. 279–282, May 1999.
- [292] D. R. Pendse and A. K. Chin, “Cathodoluminescence and Transmission Cathodoluminescence,” in *Encyclopedia of Materials: Science and Technology* (K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan, and P. Veyssi re, eds.), pp. 1–7, Oxford: Elsevier, Jan. 2001.
- [293] B. Hua, J. Motohisa, Y. Ding, S. Hara, and T. Fukui, “Characterization of Fabry-P rot microcavity modes in GaAs nanowires fabricated by selective-area metal organic vapor phase epitaxy,” *Applied Physics Letters*, vol. 91, p. 131112, Sept. 2007.
- [294] D. Saxena, S. Mokkalapati, P. Parkinson, N. Jiang, Q. Gao, H. H. Tan, and C. Jagadish, “Optically pumped room-temperature GaAs nanowire lasers,” *Nature Photonics*, vol. 7, pp. 963–968, Dec. 2013.
- [295] T. Stettner, A. Thurn, M. D binger, M. O. Hill, J. Bissinger, P. Schmiedeke, S. Matich, T. Kostenbader, D. Ruhstorfer, H. Riedl, M. Kaniber, L. J. Lauhon, J. J. Finley, and G. Koblm ller, “Tuning Lasing Emission toward Long Wavelengths in GaAs-(In,Al)GaAs Core-Multishell Nanowires,” *Nano Letters*, vol. 18, pp. 6292–6300, Oct. 2018.
- [296] S. A. Dayeh, R. Chen, Y. G. Ro, and J. Sim, “Progress in doping semiconductor nanowires during growth,” *Materials Science in Semiconductor Processing*, vol. 62, pp. 135–155, 2017.
- [297] D. E. Perea, E. R. Hemesath, E. J. Schwalbach, J. L. Lensch-Falk, P. W. Voorhees, and L. J. Lauhon, “Direct Measurement of Dopant Distribution in an Individual Vapour-liquid-solid Nanowire,” *Nat. Nanotechnol.*, vol. 4, p. 315, 2009.
- [298] W. G. Spitzer and M. B. Panish, “Silicon-Doped Gallium Arsenide Grown from Gallium Solution: Silicon Site Distribution,” *Journal of Applied Physics*, vol. 40, no. 10, pp. 4200–4202, 1969.
- [299] J. E. Northrup and S. B. Zhang, “Dopant and defect energetics: Si in GaAs,” *Physical Review B*, vol. 47, no. 11, p. 6791, 1993.

- [300] Z. Fang, E. Robin, E. Rozas-Jimenez, A. Cros, F. Donatini, N. Mollard, J. Pernot, and B. Daudin, "Silicon Donor Incorporation in GaN Nanowires," *Nano Lett.*, vol. 15, p. 6794, 2015.
- [301] C. Yang, Z. Zhong, and C. M. Lieber, "Encoding Electronic Properties by Synthesis of Axial Modulation-doped Silicon Nanowires," *Science*, vol. 310, p. 1304, 2005.
- [302] A. Patsha, S. Amirthapandian, R. Pandian, S. Bera, A. Bhattacharya, and S. Dhara, "Direct Evidence of Mg Incorporation Pathway in Vapor-Liquid-Solid Grown P-type Nonpolar GaN Nanowires," *J. Phys. Chem. C*, vol. 118, p. 24165, 2014.
- [303] I. Amit, U. Givan, J. G. Connell, D. F. Paul, J. S. Hammond, L. J. Lauhon, and Y. Rosenwaks, "Spatially Resolved Correlation of Active and Total Doping Concentrations in VLS Grown Nanowires," *Nano Lett.*, vol. 13, p. 2598, 2013.
- [304] M. Piccin, B. Bais, V. Grillo, F. Jabeen, S. De Franceschi, E. Carlino, M. Lazzarino, F. Romanato, L. Businaro, S. Rubini, F. Martelli, and A. Franciosi, "Growth by Molecular Beam Epitaxy and Electrical Characterization of GaAs Nanowires," *Phys. E*, vol. 37, p. 134, 2007.
- [305] N. Ghaderi, M. Peressi, N. Binggeli, and H. Akbarzadeh, "Structural Properties and Energetics of Intrinsic and Si-doped GaAs Nanowires: First-principles Pseudopotential Calculations," *Phys. Rev. B: Condens. Matter Mater. Phys.*, vol. 81, p. 155311, 2010.
- [306] R. E. Algra, M. A. Verheijen, M. T. Borgström, L.-F. Feiner, G. Immink, W. J. P. van Enkevort, E. Vlieg, and E. P. A. M. Bakkers, "Twinning Superlattices in Indium Phosphide Nanowires," *Nature*, vol. 456, p. 369, 2008.
- [307] J. Wallentin, K. Mergenthaler, M. Ek, L. R. Wallenberg, L. Samuelson, K. Deppert, M.-E. Pistol, and M. T. Borgström, "Probing the Wurtzite Conduction Band Structure Using State Filling in Highly Doped InP Nanowires," *Nano Lett.*, vol. 11, p. 2286, 2011.
- [308] E. R. Hemesath, D. K. Schreiber, E. B. Gulsoy, C. F. Kieselowski, A. K. Petford-Long, P. W. Voorhees, and L. J. Lauhon, "Catalyst Incorporation at Defects during Nanowire Growth," *Nano Lett.*, vol. 12, p. 167, 2012.
- [309] S. D. Hersee, X. Sun, and X. Wang, "The Controlled Growth of GaN Nanowires," *Nano Lett.*, vol. 6, p. 1808, 2006.
- [310] S. Fernandez-Garrido, X. Kong, T. Gotschke, R. Calarco, L. Geelhaar, A. Trampert, and O. Brandt, "Spontaneous Nucleation and Growth of GaN Nanowires: The Fundamental Role of Crystal Polarity," *Nano Lett.*, vol. 12, p. 6119, 2012.
- [311] H. Ghoneim, P. Mensch, H. Schmid, C. D. Bessire, R. Rhyner, A. Schenk, C. Rettner, S. Karg, K. E. Moselund, H. Riel, and M. T. Björk, "In Situ Doping of Catalyst-free InAs Nanowires," *Nanotechnology*, vol. 23, p. 505708, 2012.
- [312] F. Furtmayr, M. Vilemeyer, M. Stutzmann, J. Arbiol, S. Estrade, G. Peiro, J. R. Morante, and M. Eickhoff, "Nucleation and Growth of GaN Nanorods on Si(111) Surfaces by Plasma-assisted Molecular Beam Epitaxy: The Influence of Si- and Mg- Doping. J," *J. Appl. Phys.*, vol. 104, p. 034309, 2008.
- [313] S. Li and A. Waag, "GaN based Nanorods for Solid State Lighting," *J. Appl. Phys.*, vol. 111, p. 071101, 2012.
- [314] S. Wirths, K. Weis, K. Sladek, C. Volk, S. Alagha, T. E. Weirich, M. von der Ahe, H. Hardtdegen, H. Lüth, D. Grützmacher, and T. Schäfers, "Effect of Si-doping on InAs Nanowire Transport and Morphology," *J. Appl. Phys.*, vol. 110, p. 053709, 2011.
- [315] E. Dimakis, M. Ramsteiner, C.-N. Huang, A. Trampert, A. Davydok, A. Biermanns, U. Pietsch, H. Riechert, and L. Geelhaar, "In Situ Doping of Catalyst-free InAs Nanowires with Si: Growth, Polytypism, and Local Vibrational Modes of Si," *Appl. Phys. Lett.*, vol. 103, p. 143121, 2013.
- [316] S. Hertenberger, D. Rudolph, S. Bolte, M. Döblinger, M. Bichler, D. Spirkoska, J. J. Finley, G. Abstreiter, and G. Koblmüller, "Absence of Vapor-Liquid-Solid Growth during Molecular Beam Epitaxy of Self-induced InAs Nanowires on Si," *Appl. Phys. Lett.*, vol. 98, p. 123114, 2011.

- [317] M. Sonner, J. Treu, K. Saller, H. Riedl, J. J. Finley, and G. Koblmüller, "Carrier concentration dependent photoluminescence properties of Si-doped InAs nanowires," *Applied Physics Letters*, vol. 112, p. 091904, Feb. 2018.
- [318] V. Schmidt, P. F. J. Mensch, S. F. Karg, B. Gotsmann, P. Das Kanungo, H. Schmid, and H. Riel, "Using the Seebeck Coefficient to Determine Charge Carrier Concentration, Mobility, and Relaxation Time in InAs Nanowires," *Appl. Phys. Lett.*, vol. 104, p. 012113, 2014.
- [319] D. L. Rhode, "Electron Transport in InSb, InAs, and InP," *Phys. Rev. B*, vol. 3, p. 3287, 1971.
- [320] C. Thelander, P. Caroff, S. Plissard, A. W. Dey, and K. A. Dick, "Effects of Crystal Phase Mixing on the Electrical Properties of InAs Nanowires," *Nano Lett.*, vol. 11, p. 2424, 2011.
- [321] S. A. Dayeh, D. Susac, K. L. Kavanagh, E. T. Yu, and D. Wang, "Structural and Room-Temperature Transport Properties of Zinc Blende and Wurtzite InAs Nanowires," *Adv. Funct. Mater.*, vol. 19, p. 2102, 2009.
- [322] J. Becker, S. Morkötter, J. Treu, M. Sonner, M. Speckbacher, M. Döblinger, G. Abstreiter, J. J. Finley, and G. Koblmüller, "Carrier trapping and activation at short-period wurtzite/zinc-blende stacking sequences in polytypic InAs nanowires," *Physical Review B*, vol. 97, p. 115306, Mar. 2018.
- [323] S. Chuang, Q. Gao, R. Kapadia, A. C. Ford, J. Guo, and A. Javey, "Ballistic InAs Nanowire Transistors," *Nano Lett.*, vol. 13, p. 555, 2013.
- [324] D. M. Irber, J. Seidl, D. J. Carrad, J. Becker, N. Jeon, B. Loitsch, J. Winnerl, S. Matich, M. Döblinger, Y. Tang, S. Morkötter, G. Abstreiter, J. J. Finley, M. Grayson, L. J. Lauhon, and G. Koblmüller, "Quantum transport and sub-band structure of modulation-doped GaAs/AlAs Core-Superlattice nanowires," *Nano Lett.*, vol. 17, no. 8, pp. 4886–4893. DOI: 10.1021/acs.nanolett.7b01732, 2017.
- [325] O. Wunnicke, "Gate Capacitance of Back-gated Nanowire Field-Effect Transistors," *Appl. Phys. Lett.*, vol. 89, p. 083102, 2006.
- [326] M. Speckbacher, J. Treu, T. J. Whittles, W. M. Linhart, X. Xu, K. Saller, V. R. Dhanak, G. Abstreiter, J. J. Finley, T. D. Veal, and G. Koblmüller, "Direct Measurements of Fermi Level Pinning at the Surface of Intrinsically N-type InGaAs Nanowires," *Nano Lett.*, vol. 16, p. 5135, 2016.
- [327] C. Blömers, T. Grap, M. I. Lepsa, J. Moers, S. Trellenkamp, D. Grützmacher, H. Lüth, and T. Schäpers, "Hall effect measurements on InAs nanowires," *Applied physics letters*, vol. 101, no. 15, p. 152106, 2012. ISBN: 0003-6951 Publisher: American Institute of Physics.
- [328] V. V. Karataev, M. G. Milvidskii, N. S. Rytova, and V. I. Fistul *Sov. Phys. Semicond.*, vol. 1, p. 1718, 1977.
- [329] N. Jeon, B. Loitsch, S. Morkoetter, G. Abstreiter, J. Finley, H. J. Krenner, G. Koblmüller, and L. J. Lauhon, "Alloy Fluctuations Act as Quantum Dot-like Emitters in GaAs-AlGaAs Core-Shell Nanowires," *ACS Nano*, vol. 9, pp. 8335–8343, Aug. 2015.
- [330] D. Y. Petrovykh, M. J. Yang, and L. J. Whitman, "Chemical and Electronic Properties of Sulfur-Passivated InAs Surfaces," *Surf. Sci.*, vol. 523, p. 231, 2003.
- [331] J. Sumner, R. A. Oliver, M. J. Kappers, and C. J. Humphreys, "Scanning Capacitance Microscopy Studies of Unintentional Doping in Epitaxial Lateral Overgrowth GaN," *J. Appl. Phys.*, vol. 106, p. 104503, 2009.
- [332] A. Y. Cho and I. Hayashi, "P-N Junction Formation during Molecular-Beam Epitaxy of Ge-Doped GaAs," *Metall. Trans. A*, vol. 2, p. 777, 1971.
- [333] Y. Chai, R. Chow, and C. Wood, "The Effect of Growth Conditions on Si Incorporation in Molecular Beam Epitaxial GaAs," *Appl. Phys. Lett.*, vol. 39, p. 800, 1981.
- [334] M. Wassermeier, J. Behrend, L. Däweritz, and K. Ploog, "Reconstruction of the GaAs (001) Surface induced by Submonolayer Si Deposition," *Phys. Rev. B: Condens. Matter Mater. Phys.*, vol. 52, p. R2269, 1995.

- [335] S. Guha, N. A. Bojarczuk, and F. Cardone, “Mg in GaN: Incorporation of a Volatile Species at High Temperatures during Molecular Beam Epitaxy,” *Appl. Phys. Lett.*, vol. 71, p. 1685, 1997.
- [336] M. Galicka, R. Buczek, and P. Kacman, “Segregation of Impurities in GaAs and InAs Nanowires,” *J. Phys. Chem. C*, vol. 117, p. 20361, 2013.
- [337] G. Koblmüller and G. Abstreiter, “Growth and properties of InGaAs nanowires on silicon,” *Phys. Status Solidi RRL*, vol. 8, pp. 11–30. DOI: 10.1002/pssr.201308207, 2014. tex.publisher: Wiley Online Library.
- [338] H. Kim, W.-J. Lee, A. C. Farrell, J. S. Morales, P. N. Senanayake, S. V. Prikhodko, T. Ochalski, and D. L. Huffaker, “Monolithic InGaAs nanowire array lasers on silicon-on-insulator operating at room temperature,” *Nano Lett.*, vol. 17, no. 6, pp. 3465–3470. DOI: 10.1021/acs.nanolett.7b00384, 2017.
- [339] L. Shen, E. Y. Pun, and J. C. Ho, “Recent developments in III-V semiconducting nanowires for high-performance photodetectors,” *Mater. Chem. Front.*, vol. 1, no. 4, pp. 630–645. DOI: 10.1039/C6QM00279J, 2017.
- [340] N. Li, K. Liu, V. J. Sorger, and D. K. Sadana, “Monolithic III-V on silicon plasmonic nanolaser structure for optical interconnects,” *Sci. Rep.*, vol. 5, p. 14067. DOI: 10.1038/srep14067, 2015.
- [341] T. Mårtensson, C. P. T. Svensson, B. A. Wacaser, M. W. Larsson, W. Seifert, K. Deppert, A. Gustafsson, L. R. Wallenberg, and L. Samuelson, “Epitaxial III-V nanowires on silicon,” *Nano Lett.*, vol. 4, no. 10, pp. 1987–1990. DOI: 10.1021/nl0487267, 2004. tex.publisher: ACS Publications.
- [342] R. LaPierre, M. Robson, K. Azizur-Rahman, and P. Kuyanov, “A review of III-V nanowire infrared photodetectors and sensors,” *J. Phys. D Appl. Phys.*, vol. 50, no. 12, pp. 123001. DOI: 10.1088/1361-6463/aa5ab3, 2017.
- [343] N. Jeon, B. Loitsch, S. Morkötter, G. Abstreiter, J. Finley, H. J. Krenner, G. Koblmüller, and L. J. Lauhon, “Alloy fluctuations act as quantum dot-like emitters in GaAs-AlGaAs core-shell nanowires,” *ACS Nano*, vol. 9, pp. 8335–8343. DOI: 10.1021/acsnano.5b04070, Aug. 2015.
- [344] U. Jahn, J. Lähnemann, C. Pfüller, O. Brandt, S. Breuer, B. Jenichen, M. Ramsteiner, L. Geelhaar, and H. Riechert, “Luminescence of GaAs nanowires consisting of wurtzite and zinc-blende segments,” *Phys. Rev. B*, vol. 85, no. 4, p. 045323. DOI: 10.1103/PhysRevB.85.045323, 2012. tex.publisher: APS.
- [345] A. Davtyan, T. Krause, D. Kriegner, A. Al-Hassan, D. Bahrami, S. Mostafavi Kashani, R. B. Lewis, H. Küpers, A. Tahraoui, and L. Geelhaar, “Threefold rotational symmetry in hexagonally shaped core-shell (In, Ga) As/GaAs nanowires revealed by coherent X-ray diffraction imaging,” *J. Appl. Crystallogr.*, vol. 50, no. 3, pp. 673–680. DOI: 10.1107/S1600576717004149, 2017. tex.publisher: International Union of Crystallography.
- [346] A. Diaz, C. Mocuta, J. Stangl, B. Mandl, C. David, J. Vila-Comamala, V. Chamard, T. Metzger, and G. Bauer, “Coherent diffraction imaging of a single epitaxial InAs nanowire using a focused x-ray beam,” *Phys. Rev. B*, vol. 79, p. 125324. DOI: 10.1103/PhysRevB.79.125324, Mar. 2009.
- [347] S. Labat, M.-I. Richard, M. Dupraz, M. Gailhanou, G. Beutier, M. Verdier, F. Mastropietro, T. W. Cornelius, T. U. Schüllli, J. Eymery, and O. Thomas, “Inversion domain boundaries in GaN wires revealed by coherent bragg imaging,” *ACS Nano*, vol. 9, pp. 9210–9216. DOI: 10.1021/acsnano.5b03857, Sept. 2015.
- [348] A. Davtyan, A. Biermanns, O. Löffeld, and U. Pietsch, “Determination of the stacking fault density in highly defective single GaAs nanowires by means of coherent diffraction imaging,” *New J. Phys.*, vol. 18, no. 6, pp. 063021. DOI: 10.1088/1367-2630/18/6/063021, 2016. tex.publisher: IOP Publishing.
- [349] A. Davtyan, S. Lehmann, D. Kriegner, R. R. Zamani, K. A. Dick, D. Bahrami, A. Al-Hassan, S. J. Leake, U. Pietsch, and V. Holý, “Characterization of individual stacking faults in a wurtzite GaAs nanowire by nanobeam X-ray diffraction,” *J. Synchrotron Radiat.*, vol. 24, no. 5, pp. 981–990. DOI:

- 10.1107/S1600577517009584, 2017. tex.publisher: International Union of Crystallography.
- [350] J. Treu, T. Stettner, M. Watzinger, S. Morkötter, M. Doeblinger, S. Matich, K. Saller, M. Bichler, G. Abstreiter, J. J. Finley, J. Stangl, and G. Koblmüller, “Lattice-matched InGaAs-InAlAs core-shell nanowires with improved luminescence and photoresponse properties,” *Nano Lett.*, vol. 15, pp. 3533–3540. DOI: 10.1021/acs.nanolett.5b00979, May 2015.
 - [351] P. Godard, G. Carbone, M. Allain, F. Mastropietro, G. Chen, L. Capello, A. Diaz, T. H. Metzger, J. Stangl, and V. Chamard, “Three-dimensional high-resolution quantitative microscopy of extended crystals,” *Nat. Commun.*, vol. 2, p. 568. DOI: 10.1038/ncomms1569, 2011.
 - [352] J. M. Rodenburg, A. C. Hurst, A. G. Cullis, B. R. Dobson, F. Pfeiffer, O. Bunk, C. David, K. Jefimovs, and I. Johnson, “Hard-x-ray lensless imaging of extended objects,” *Phys. Rev. Lett.*, vol. 98, no. 3, p. 034801. DOI: 10.1103/PhysRevLett.98.034801, 2007.
 - [353] P. Thibault, M. Dierolf, A. Menzel, O. Bunk, C. David, and F. Pfeiffer, “High-resolution scanning x-ray diffraction microscopy,” *Science*, vol. 321, pp. 379–382. DOI: 10.1126/science.1158573, July 2008.
 - [354] P. Godard, M. Allain, V. Chamard, and J. Rodenburg, “Noise models for low counting rate coherent diffraction imaging,” *Opt. Express*, vol. 20, no. 23, pp. 25914–25934. DOI: 10.1126/science.1158573, 2012.
 - [355] M. V. Holt, S. O. Hruszkewycz, C. E. Murray, J. R. Holt, D. M. Paskiewicz, and P. H. Fuoss, “Strain Imaging of Nanoscale Semiconductor Heterostructures with X-Ray Bragg Projection Ptychography,” *Physical Review Letters*, vol. 112, p. 165502, Apr. 2014.
 - [356] A. Munkholm, C. Thompson, C. M. Foster, J. A. Eastman, O. Auciello, G. B. Stephenson, P. Fini, S. P. DenBaars, and J. S. Speck, “Determination of the cubic to hexagonal fraction in GaN nucleation layers using grazing incidence x-ray scattering,” *Appl. Phys. Lett.*, vol. 72, no. 23, pp. 2972–4. DOI: 10.1063/1.121511, 1998.
 - [357] Y. Takahashi, A. Suzuki, S. Furutaku, K. Yamauchi, Y. Kohmura, and T. Ishikawa, “Bragg x-ray ptychography of a silicon crystal: Visualization of the dislocation strain field and the production of a vortex beam,” *Phys. Rev. B*, vol. 87, p. 121201. DOI: 10.1103/PhysRevB.87.121201, Mar. 2013.
 - [358] S. O. Hruszkewycz, M. J. Highland, M. V. Holt, D. Kim, C. M. Folkman, C. Thompson, A. Tripathi, G. B. Stephenson, S. Hong, and P. H. Fuoss, “Imaging local polarization in ferroelectric thin films by coherent x-ray bragg projection ptychography,” *Phys. Rev. Lett.*, vol. 110, p. 177601. DOI: 10.1103/PhysRevLett.110.177601, Apr. 2013.
 - [359] A. I. Pateras, M. Allain, P. Godard, L. Largeau, G. Patriarche, A. Talneau, K. Pantzas, M. Burghammer, A. A. Minkevich, and V. Chamard, “Nondestructive three-dimensional imaging of crystal strain and rotations in an extended bonded semiconductor heterostructure,” *Phys. Rev. B*, vol. 92, pp. 205305–11. DOI: 10.1103/PhysRevB.92.205305, Nov. 2015.
 - [360] P. M. Pelz, M. Guizar-Sicairos, P. Thibault, I. Johnson, M. Holler, and A. Menzel, “On-the-fly scans for X-ray ptychography,” *Appl. Phys. Lett.*, vol. 105, no. 25, p. 251101. DOI: 10.1063/1.4904943, 2014.
 - [361] J. N. Clark, X. Huang, R. J. Harder, and I. K. Robinson, “Continuous scanning mode for ptychography,” *Opt. Lett.*, vol. 39, no. 20, pp. 6066–6069. DOI: 10.1364/OL.39.006066P, 2014. tex.publisher: Optical Society of America.
 - [362] S. Morkötter, S. Funk, M. Liang, M. Doeblinger, S. Hertenberger, J. Treu, D. Rudolph, A. Yadav, J. Becker, M. Bichler, G. Scarpa, P. Lugli, I. Zardo, J. J. Finley, G. Abstreiter, and G. Koblmüller, “Role of microstructure on optical properties in high-uniformity In_{1-x}Ga_xAs nanowire arrays: Evidence of a wider wurtzite band gap,” *Phys. Rev. B*, vol. 87, p. 205303. DOI: 10.1103/PhysRevB.87.205303, 2013.
 - [363] H. Yan, E. Nazaretski, K. Lauer, X. Huang, U. Wagner, C. Rau, M. Yusuf, I. Robinson, S. Kalbfleisch, and L. Li, “Multimodality hard-x-ray imaging of a chromosome with nanoscale

- spatial resolution,” *Sci. Rep.*, vol. 6, p. 20112. DOI: 10.1038/srep20112, 2016.
- [364] E. Nazaretski, K. Lauer, H. Yan, N. Bouet, J. Zhou, R. Conley, X. Huang, W. Xu, M. Lu, K. Gofron, S. Kalbfleisch, U. Wagner, C. Rau, and Y. S. Chu, “Pushing the limits: an instrument for hard X-ray imaging below 20 nm,” *J. Synchrotron Radiat.*, vol. 22, pp. 1–6. DOI: 10.1107/S1600577514025715, 2015.
 - [365] E. Nazaretski, H. Yan, K. Lauer, N. Bouet, X. Huang, W. Xu, J. Zhou, D. Shu, Y. Hwu, Y. S. Chu, and i. press), “Design and performance of an x-ray scanning microscope at the Hard X-ray Nanoprobe Beamline of the NSLS-II,” *J. Synchrotron Radiat.*, 2017.
 - [366] V. Favre-Nicolin, F. Mastropietro, J. Eymery, D. Camacho, Y. M. Niquet, B. M. Borg, M. E. Messing, L.-E. Wernersson, R. E. Algra, E. P. A. M. Bakkers, T. H. Metzger, R. Harder, and I. K. Robinson, “Analysis of strain and stacking faults in single nanowires using Bragg coherent diffraction imaging,” *New J. Phys.*, vol. 12, pp. 035013. DOI:10.1088/1367-2630/12/3/035013, Mar. 2010.
 - [367] S. O. Hruszkewycz, M. V. Holt, M. Allain, V. Chamard, S. M. Polvino, C. E. Murray, and P. H. Fuoss, “Efficient modeling of Bragg coherent x-ray nanobeam diffraction,” *Opt. Lett.*, vol. 40, no. 14, p. 3241. DOI: 10.1364/OL.40.003241, 2015.
 - [368] D. Dzhigaev, A. Shabalin, T. Stankevič, U. Lorenz, R. Kurta, F. Seiboth, J. Wallentin, A. Singer, S. Lazarev, O. Yefanov, and I. A. Vartanyants, “Bragg coherent x-ray diffractive imaging of a single indium phosphide nanowire,” *J. Opt.*, vol. 18, no. 6, pp. 064007. DOI: 10.1088/2040-8978/18/6/064007, 2016.
 - [369] H. Wallander and J. Wallentin, “Simulated sample heating from a nanofocused X-ray beam,” *J. Synchrotron Radiat.*, vol. 24, no. 5, pp. 925–933. DOI: 10.1107/S1600577517008712, 2017. tex.publisher: International Union of Crystallography.
 - [370] A. Ulvestad, A. Singer, J. N. Clark, H. M. Cho, J. W. Kim, R. Harder, J. Maser, Y. S. Meng, and O. G. Shpyrko, “Topological defect dynamics in operando battery nanoparticles,” *Science*, vol. 348, no. 6241, pp. 1344–1347. DOI: 10.1126/science.aaa1313, 2015.
 - [371] F. Mastropietro, P. Godard, M. Burghammer, C. Chevallard, J. Daillant, J. Duboisset, M. Allain, P. Guenoun, J. Nouet, and V. Chamard, “Revealing crystalline domains in a mollusc shell single-crystalline prism,” *Nat. Mater.*, vol. 9, pp. 946–952. DOI: 10.1038/nmat4937, 2017.
 - [372] D. Dzhigaev, T. Stankevič, I. Besedin, S. Lazarev, A. Shabalin, M. N. Strikhanov, R. Feidenhans, and I. A. Vartanyants, “Theoretical analysis of the strain mapping in a single core-shell nanowire by x-ray Bragg ptychography,” *Proc. SPIE*, vol. 9592, pp. 95920S–95920S. DOI: 10.1117/12.2190416, 2015. tex.organization: International Society for Optics and Photonics.
 - [373] I. Calvo-Almazán, M. Allain, S. Maddali, V. Chamard, and S. O. Hruszkewycz, “Impact and mitigation of angular uncertainties in Bragg coherent x-ray diffraction imaging,” *Scientific Reports*, vol. 9, pp. 1–7, Apr. 2019.
 - [374] A. M. Maiden, M. J. Humphry, M. C. Sarahan, B. Kraus, and J. M. Rodenburg, “An annealing algorithm to correct positioning errors in ptychography,” *Ultramicroscopy*, vol. 120, pp. 64–72, Sept. 2012.
 - [375] L. Lötgering, M. Rose, K. Keskinbora, M. Baluktsian, G. Dogan, U. Sanli, I. Bykova, M. Weigand, G. Schütz, and T. Wilhein, “Correction of axial position uncertainty and systematic detector errors in ptychographic diffraction imaging,” *Optical Engineering*, vol. 57, p. 084106, Aug. 2018.
 - [376] A. F. i. Morral, D. Spirkoska, J. Arbiol, M. Heigoldt, J. R. Morante, and G. Abstreiter, “Prismatic Quantum Heterostructures Synthesized on Molecular-Beam Epitaxy GaAs Nanowires,” *Small*, vol. 4, pp. 899–903, July 2008.
 - [377] X. Dai, S. Zhang, Z. Wang, G. Adamo, H. Liu, Y. Huang, C. Couteau, and C. Soci, “GaAs/AlGaAs Nanowire Photodetector,” *Nano Letters*, vol. 14, pp. 2688–2693, May 2014.

- [378] J. Treu, T. Stettner, M. Watzinger, S. Morkötter, M. Döblinger, S. Matich, K. Saller, M. Bichler, G. Abstreiter, J. J. Finley, J. Stangl, and G. Koblmüller, "Lattice-Matched InGaAs-InAlAs Core-Shell Nanowires with Improved Luminescence and Photoresponse Properties," *Nano Letters*, vol. 15, pp. 3533–3540, May 2015.
- [379] N. Erhard, S. Zenger, S. Morkötter, D. Rudolph, M. Weiss, H. J. Krenner, H. Karl, G. Abstreiter, J. J. Finley, G. Koblmüller, and A. W. Holleitner, "Ultrafast Photodetection in the Quantum Wells of Single AlGaAs/GaAs-Based Nanowires," *Nano Letters*, vol. 15, pp. 6869–6874, Oct. 2015.
- [380] K. Moratis, S. L. Tan, S. Germanis, C. Katsidis, M. Androulidaki, K. Tsagaraki, Z. Hatzopoulos, F. Donatini, J. Cibert, Y. M. Niquet, H. Mariette, and N. T. Pelekanos, "Strained GaAs/InGaAs Core-Shell Nanowires for Photovoltaic Applications," *Nanoscale Research Letters*, vol. 11, Dec. 2016.
- [381] H. Kim, W.-J. Lee, A. C. Farrell, A. Balgarkashi, and D. L. Huffaker, "Telecom-Wavelength Bottom-up Nanobeam Lasers on Silicon-on-Insulator," *Nano Letters*, vol. 17, pp. 5244–5250, Sept. 2017.
- [382] R. Chen, K. W. Ng, W. S. Ko, D. Parekh, F. Lu, T.-T. D. Tran, K. Li, and C. Chang-Hasnain, "Nanophotonic integrated circuits from nanoresonators grown on silicon," *Nature Communications*, vol. 5, Dec. 2014.
- [383] I. Giunttoni, L. Geelhaar, J. Bruns, and H. Riechert, "Light coupling between vertical III-As nanowires and planar Si photonic waveguides for the monolithic integration of active optoelectronic devices on a Si platform," *Optics Express*, vol. 24, p. 18417, Aug. 2016.
- [384] H. Kim, W.-J. Lee, A. C. Farrell, J. S. D. Morales, P. Senanayake, S. V. Prikhodko, T. J. Ochalski, and D. L. Huffaker, "Monolithic InGaAs Nanowire Array Lasers on Silicon-on-Insulator Operating at Room Temperature," *Nano Letters*, vol. 17, pp. 3465–3470, June 2017.
- [385] M. Koguchi, H. Kakibayashi, M. Yazawa, K. Hiruma, and T. Katsuyama, "Crystal Structure Change of GaAs and InAs Whiskers from Zinc-Blende to Wurtzite Type," *Japanese Journal of Applied Physics*, vol. 31, pp. 2061–2065, July 1992.
- [386] A. I. Persson, M. W. Larsson, S. Stenström, B. J. Ohlsson, L. Samuelson, and L. R. Wallenberg, "Solid-phase diffusion mechanism for GaAs nanowire growth," *Nature Materials*, vol. 3, pp. 677–681, Oct. 2004.
- [387] U. Jahn, J. Lähnemann, C. Pfüller, O. Brandt, S. Breuer, B. Jenichen, M. Ramsteiner, L. Geelhaar, and H. Riechert, "Luminescence of GaAs nanowires consisting of wurtzite and zinc-blende segments," *Physical Review B*, vol. 85, p. 045323, Jan. 2012. `tex.arxiv= 1201.6540 tex.bibcode= 2012PhRvB..85d5323J tex.issue= 4 tex.numpages= 7 tex.owner= jonas`.
- [388] D. Jacobsson, F. Panciera, J. Tersoff, M. C. Reuter, S. Lehmann, S. Hofmann, K. A. Dick, and F. M. Ross, "Interface dynamics and crystal phase switching in GaAs nanowires," *Nature*, vol. 531, pp. 317–322, Mar. 2016.
- [389] S. Lehmann, D. Jacobsson, K. Deppert, and K. A. Dick, "High crystal quality wurtzite-zinc blende heterostructures in metal-organic vapor phase epitaxy-grown GaAs nanowires," *Nano Research*, vol. 5, pp. 470–476, July 2012.
- [390] P. Kusch, E. Grelich, C. Somaschini, E. Luna, M. Ramsteiner, L. Geelhaar, H. Riechert, and S. Reich, "Type-II band alignment of zinc-blende and wurtzite segments in GaAs nanowires: A combined photoluminescence and resonant Raman scattering study," *Physical Review B*, vol. 89, p. 045310, Jan. 2014.
- [391] M. B. Rota, A. S. Ameruddin, H. A. Fonseka, Q. Gao, F. Mura, A. Polimeni, A. Miriametro, H. H. Tan, C. Jagadish, and M. Capizzi, "Bandgap Energy of Wurtzite InAs Nanowires," *Nano Letters*, vol. 16, pp. 5197–5203, Aug. 2016.
- [392] S. Morkötter, S. Funk, M. Liang, M. Döblinger, S. Hertenberger, J. Treu, D. Rudolph, A. Yadav, J. Becker, M. Bichler, G. Scarpa, P. Lugli, I. Zardo, J. J. Finley, G. Abstreiter, and

- G. Koblmüller, "Role of microstructure on optical properties in high-uniformity $\text{In}_{1-x}\text{Ga}_x\text{As}$ nanowire arrays: Evidence of a wider wurtzite band gap," *Physical Review B*, vol. 87, p. 205303, May 2013.
- [393] A. Davtyan, T. Krause, D. Kriegner, A. Al-Hassan, D. Bahrami, S. M. Mostafavi Kashani, R. B. Lewis, H. Küpers, A. Tahraoui, L. Geelhaar, M. Hanke, S. J. Leake, O. Loffeld, and U. Pietsch, "Threefold rotational symmetry in hexagonally shaped core-shell (In,Ga)As/GaAs nanowires revealed by coherent X-ray diffraction imaging," *Journal of Applied Crystallography*, vol. 50, pp. 673–680, June 2017.
- [394] R. B. Lewis, L. Nicolai, H. Küpers, M. Ramsteiner, A. Trampert, and L. Geelhaar, "Anomalous Strain Relaxation in Core-Shell Nanowire Heterostructures via Simultaneous Coherent and Incoherent Growth," *Nano Letters*, vol. 17, pp. 136–142, Jan. 2017.
- [395] M. Paladugu, J. Zou, Y. N. Guo, X. Zhang, H. J. Joyce, Q. Gao, H. H. Tan, C. Jagadish, and Y. Kim, "Evolution of Wurtzite Structured GaAs Shells Around InAs Nanowire Cores," *Nanoscale Research Letters*, vol. 4, pp. 846–849, May 2009.
- [396] P. Corfdir, R. B. Lewis, O. Marquardt, H. Küpers, J. Grandal, E. Dimakis, A. Trampert, L. Geelhaar, O. Brandt, and R. T. Phillips, "Exciton recombination at crystal-phase quantum rings in GaAs/In_xGa_{1-x}As core/multishell nanowires," *Applied Physics Letters*, vol. 109, p. 082107, Aug. 2016.
- [397] C. Colombo, D. Spirkoska, M. Frimmer, G. Abstreiter, and A. Fontcuberta i Morral, "Ga-assisted catalyst-free growth mechanism of GaAs nanowires by molecular beam epitaxy," *Physical Review B*, vol. 77, p. 155326, Apr. 2008.
- [398] F. Jabeen, V. Grillo, S. Rubini, and F. Martelli, "Self-catalyzed growth of GaAs nanowires on cleaved Si by molecular beam epitaxy," *Nanotechnology*, vol. 19, no. 27, p. 275711, 2008.
- [399] J. Lähnemann, M. O. Hill, J. Herranz, O. Marquardt, G. Gao, A. Al Hassan, A. Davtyan, S. O. Hruszkewycz, M. V. Holt, C. Huang, I. Calvo-Almazán, U. Jahn, U. Pietsch, L. J. Lauhon, and L. Geelhaar, "Correlated Nanoscale Analysis of the Emission from Wurtzite versus Zincblende (In,Ga)As/GaAs Nanowire Core-Shell Quantum Wells," *Nano Letters*, vol. 19, pp. 4448–4457, July 2019.
- [400] X. Yu, H. Wang, J. Lu, J. Zhao, J. Misuraca, P. Xiong, and S. von Molnár, "Evidence for Structural Phase Transitions Induced by the Triple Phase Line Shift in Self-Catalyzed GaAs Nanowires," *Nano Letters*, vol. 12, pp. 5436–5442, Oct. 2012.
- [401] M. H. T. Dastjerdi, J. P. Boulanger, P. Kuyanov, M. Aagesen, and R. R. LaPierre, "Methods of Ga droplet consumption for improved GaAs nanowire solar cell efficiency," *Nanotechnology*, vol. 27, p. 475403, Nov. 2016.
- [402] S. Plissard, K. A. Dick, G. Larrieu, S. Godey, A. Addad, X. Wallart, and Philippe Caroff, "Gold-free growth of GaAs nanowires on silicon: arrays and polytypism," *Nanotechnology*, vol. 21, no. 38, p. 385602, 2010.
- [403] M. O. Hill, I. Calvo-Almazan, M. Allain, M. V. Holt, A. Ulvestad, J. Treu, G. Koblmüller, C. Huang, X. Huang, H. Yan, E. Nazaretski, Y. S. Chu, G. B. Stephenson, V. Chamard, L. J. Lauhon, and S. O. Hruszkewycz, "Measuring Three-Dimensional Strain and Structural Defects in a Single InGaAs Nanowire Using Coherent X-ray Multiangle Bragg Projection Ptychography," *Nano Letters*, vol. 18, pp. 811–819, Feb. 2018.
- [404] V. Favre-Nicolin, F. Mastropietro, J. Eymery, D. Camacho, Y. M. Niquet, B. M. Borg, M. E. Messing, L.-E. Wernersson, R. E. Algra, E. P. A. M. Bakkers, T. H. Metzger, R. Harder, and I. K. Robinson, "Analysis of strain and stacking faults in single nanowires using Bragg coherent diffraction imaging," *New Journal of Physics*, vol. 12, no. 3, p. 035013, 2010.
- [405] H. Hillmer, A. Forchel, S. Hansmann, M. Morohashi, E. Lopez, H. P. Meier, and K. Ploog, "Optical investigations on the mobility of two-dimensional excitons in GaAs/ Ga_{1-x}Al_xAs quantum

- wells,” *Physical Review B*, vol. 39, pp. 10901–10912, May 1989.
- [406] M. Pieczarka, M. Syperek, D. Biegańska, C. Gilfert, E. M. Pavelescu, J. P. Reithmaier, J. Misiewicz, and G. Sek, “Lateral carrier diffusion in InGaAs/GaAs coupled quantum dot-quantum well system,” *Applied Physics Letters*, vol. 110, p. 221104, May 2017.
 - [407] F. Bechstedt and A. Belabbes, “Structure, energetics, and electronic states of III–V compound polytypes,” *Journal of Physics: Condensed Matter*, vol. 25, p. 273201, July 2013.
 - [408] O. Marquardt, M. Ramsteiner, P. Corfdir, L. Geelhaar, and O. Brandt, “Modeling the electronic properties of GaAs polytype nanostructures: Impact of strain on the conduction band character,” *Physical Review B*, vol. 95, p. 245309, June 2017.
 - [409] L. Rigutti, L. Mancini, D. Hernández-Maldonado, W. Lefebvre, E. Giraud, R. Butté, J. F. Carlin, N. Grandjean, D. Blavette, and F. Vurpillot, “Statistical correction of atom probe tomography data of semiconductor alloys combined with optical spectroscopy: The case of Al_{0.25}Ga_{0.75}N,” *Journal of Applied Physics*, vol. 119, p. 105704, Mar. 2016.
 - [410] J. R. Riley, T. Detchprohm, C. Wetzel, and L. J. Lauhon, “On the reliable analysis of indium mole fraction within In_xGa_{1-x}N quantum wells using atom probe tomography,” *Applied Physics Letters*, vol. 104, p. 152102, Apr. 2014.
 - [411] T. Rieger, T. Schäpers, D. Grützmacher, and M. I. Lepsa, “Crystal Phase Selective Growth in GaAs/InAs Core–Shell Nanowires,” *Crystal Growth & Design*, vol. 14, pp. 1167–1174, Mar. 2014.
 - [412] S. G. Ghalamestani, M. Heurlin, L.-E. Wernersson, S. Lehmann, and K. A. Dick, “Growth of InAs/InP core–shell nanowires with various pure crystal structures,” *Nanotechnology*, vol. 23, p. 285601, July 2012.
 - [413] S. G. Ghalamestani, A. Mazid Munshi, D. L. Dheeraj, B.-O. Fimland, H. Weman, and K. A. Dick, “Self-catalyzed MBE grown GaAs/GaAs_xSb_{1-x} core–shell nanowires in ZB and WZ crystal structures,” *Nanotechnology*, vol. 24, p. 405601, Oct. 2013.
 - [414] T. Stankevič, E. Hilner, F. Seiboth, R. Ciechonski, G. Vescovi, O. Kryliouk, U. Johansson, L. Samuelson, G. Wellenreuther, G. Falkenberg, R. Feidenhans’l, and A. Mikkelsen, “Fast Strain Mapping of Nanowire Light-Emitting Diodes Using Nanofocused X-ray Beams,” *ACS Nano*, vol. 9, pp. 6978–6984, July 2015.
 - [415] A. Biermanns, S. Breuer, A. Davydok, L. Geelhaar, and U. Pietsch, “Structural polytypism and residual strain in GaAs nanowires grown on Si(111) probed by single-nanowire X-ray diffraction,” *Journal of Applied Crystallography*, vol. 45, pp. 239–244, Apr. 2012.
 - [416] G. Signorello, S. Karg, M. T. Björk, B. Gotsmann, and H. Riel, “Tuning the Light Emission from GaAs Nanowires over 290 meV with Uniaxial Strain,” *Nano Letters*, vol. 13, pp. 917–924, Mar. 2013.
 - [417] G. Signorello, E. Lörtscher, P. Khomyakov, S. Karg, D. Dheeraj, B. Gotsmann, H. Weman, and H. Riel, “Inducing a direct-to-pseudodirect bandgap transition in wurtzite GaAs nanowires with uniaxial stress,” *Nature Communications*, vol. 5, p. 3655, Dec. 2014.
 - [418] H. Küpers, F. Bastiman, E. Luna, C. Somaschini, and L. Geelhaar, “Ga predeposition for the Ga-assisted growth of GaAs nanowire ensembles with low number density and homogeneous length,” *Journal of Crystal Growth*, vol. 459, pp. 43–49, Feb. 2017.
 - [419] F. Bastiman, H. Küpers, C. Somaschini, and L. Geelhaar, “Growth map for Ga-assisted growth of GaAs nanowires on Si(111) substrates by molecular beam epitaxy,” *Nanotechnology*, vol. 27, p. 095601, Mar. 2016.
 - [420] W.-H. Lin, U. Jahn, H. Küpers, E. Luna, R. B. Lewis, L. Geelhaar, and O. Brandt, “Efficient methodology to correlate structural with optical properties of GaAs nanowires based on scanning electron microscopy,” *Nanotechnology*, vol. 28, p. 415703, Oct. 2017.

- [421] F. D. L. Peña, T. Ostasevicius, V. T. Fauske, P. Burdet, E. Prestat, P. Jokubauskas, M. Nord, K. E. MacArthur, M. Sarahan, D. N. Johnstone, J. Taillon, A. Eljarrat, V. Migunov, J. Caron, T. Furnival, S. Mazzucco, T. Aarholt, M. Walls, T. Slater, F. Winkler, B. Martineau, G. Donval, R. McLeod, E. R. Hoglund, I. Alxneit, I. Hjorth, T. Henninen, Luiz Fernando Zagonel, A. Garmannslund, and 5ht2, “Hyperspy 1.4,” Sept. 2018.
- [422] S. Koelling, A. Li, A. Cavalli, S. Assali, D. Car, S. Gazibegovic, E. P. A. M. Bakkers, and P. M. Koenraad, “Atom-by-Atom Analysis of Semiconductor Nanowires with Parts Per Million Sensitivity,” *Nano Letters*, vol. 17, pp. 599–605, Feb. 2017.
- [423] L. C. Lew Yan Voon and M. Willatzen, *The $\mathbf{k} \cdot \mathbf{p}$ Method: electronic properties of semiconductors*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2009. Citation Key Alias: LewYanVoon_2009a, LewYanVoon_2009b.
- [424] O. Marquardt, S. Boeck, C. Freysoldt, T. Hickel, S. Schulz, J. Neugebauer, and E. P. O’Reilly, “A generalized plane-wave formulation of $\mathbf{k} \cdot \mathbf{p}$ formalism and continuum-elasticity approach to elastic and electronic properties of semiconductor nanostructures,” *Computational Materials Science*, vol. 95, pp. 280–287, Dec. 2014.
- [425] S. L. Chuang and C. S. Chang, “ $\mathbf{k} \cdot \mathbf{p}$ method for strained wurtzite semiconductors,” *Physical Review B*, vol. 54, pp. 2491–2504, July 1996.
- [426] J. I. Climente, C. Segarra, F. Rajadell, and J. Planelles, “Electrons, holes, and excitons in GaAs polytype quantum dots,” *Journal of Applied Physics*, vol. 119, p. 125705, Mar. 2016.
- [427] Y. Fu and K. A. Chao, “Exciton binding energy in $\{\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}\}$ multiple quantum wells,” *Physical Review B*, vol. 43, pp. 12626–12629, May 1991.
- [428] N. Jeon, D. Ruhstorfer, M. Döblinger, S. Matich, B. Loitsch, G. Koblmüller, and L. Lauhon, “Connecting Composition-Driven Faceting with Facet-Driven Composition Modulation in GaAs–AlGaAs Core–Shell Nanowires,” *Nano Letters*, vol. 18, pp. 5179–5185, Aug. 2018.
- [429] A. AlHassan, J. Lähnemann, S. Leake, H. Küpers, M. Niehle, D. Bahrami, F. Bertram, R. B. Lewis, A. Davtyan, T. U. Schüllli, L. Geelhaar, and U. Pietsch, “Spatially-resolved luminescence and crystal structure of single core–shell nanowires measured in the as-grown geometry,” *Nanotechnology*, vol. 31, p. 214002, Mar. 2020.
- [430] M. M. Sonner, A. Sitek, L. Janker, D. Rudolph, D. Ruhstorfer, M. Döblinger, A. Manolescu, G. Abstreiter, J. J. Finley, A. Wixforth, G. Koblmüller, and H. J. Krenner, “Breakdown of Corner States and Carrier Localization by Monolayer Fluctuations in Radial Nanowire Quantum Wells,” *Nano Letters*, vol. 19, pp. 3336–3343, May 2019.
- [431] G. C. DeSalvo, W. F. Tseng, and J. Comas, “Etch rates and selectivities of citric acid/hydrogen peroxide on GaAs, Al_{0.3}Ga_{0.7}As, In_{0.2}Ga_{0.8}As, In_{0.53}Ga_{0.47}As, In_{0.52}Al_{0.48}As, and InP,” *Journal of The Electrochemical Society*, vol. 139, no. 3, p. 831, 1992.
- [432] J. C. H. Spence, U. Weierstall, and M. Howells, “Coherence and sampling requirements for diffractive imaging,” *Ultramicroscopy*, vol. 101, pp. 149–152, Nov. 2004.
- [433] S. Maddali, “siddharth-maddali/Phaser,” Apr. 2020.
- [434] S. Maddali, P. Li, A. Pateras, D. Timbie, N. Deegan, A. L. Crook, H. Lee, I. Calvo-Almazan, D. Sheyfer, W. Cha, F. J. Heremans, D. D. Awschalom, V. Chamard, M. Allain, and S. O. Hruszkewycz, “General approaches for shear-correcting coordinate transformations in Bragg coherent diffraction imaging. Part I,” *Journal of Applied Crystallography*, vol. 53, pp. 393–403, Apr. 2020.
- [435] P. Li, S. Maddali, A. Pateras, I. Calvo-Almazan, S. O. Hruszkewycz, W. Cha, V. Chamard, and M. Allain, “General approaches for shear-correcting coordinate transformations in Bragg coherent diffraction imaging. Part II,” *Journal of Applied Crystallography*, vol. 53, pp. 404–418, Apr. 2020.
- [436] R. Popovitz-Biro, A. Kretinin, P. Von Huth, and H. Shtrikman, “InAs/GaAs core–shell nanowires,” *Crystal growth & design*, vol. 11, no. 9, pp. 3858–3865, 2011.

- [437] P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert, and L. Samuelson, "Controlled polytypic and twin-plane superlattices in iii-v nanowires," *Nature Nanotechnology*, vol. 4, pp. 50–55, Jan. 2009. Number: 1 Publisher: Nature Publishing Group.
- [438] K. Yoon, J. K. Hyun, J. G. Connell, I. Amit, Y. Rosenwaks, and L. J. Lauhon, "Barrier Height Measurement of Metal Contacts to Si Nanowires Using Internal Photoemission of Hot Carriers," *Nano Letters*, vol. 13, pp. 6183–6188, Dec. 2013.
- [439] R. A. Schlitz, D. E. Perea, J. L. Lensch-Falk, E. R. Hemesath, and L. J. Lauhon, "Correlating dopant distributions and electrical properties of boron-doped silicon nanowires," *Applied Physics Letters*, vol. 95, p. 162101, Oct. 2009.
- [440] E. Mohapatra, T. P. Dash, J. Jena, S. Das, and C. K. Maiti, "Strain induced variability study in Gate-All-Around vertically-stacked horizontal nanosheet transistors," *Physica Scripta*, vol. 95, p. 065808, May 2020.
- [441] P. Favia, O. Richard, G. Eneman, H. Mertens, H. Arimura, E. Capogreco, A. Hikavyy, L. Witters, P. Kundu, R. Loo, E. Vancoille, and H. Bender, "TEM investigations of gate-all-around nanowire devices," *Semiconductor Science and Technology*, vol. 34, p. 124003, Nov. 2019. Publisher: IOP Publishing.
- [442] M. Friedl, K. Cervený, P. Weigle, G. Tütüncüoğlu, S. Martí-Sánchez, C. Huang, T. Patlatiuk, H. Potts, Z. Sun, M. O. Hill, L. Güniat, W. Kim, M. Zamani, V. G. Dubrovskii, J. Arbiol, L. J. Lauhon, D. M. Zumbühl, and A. Fontcuberta i Morral, "Template-Assisted Scalable Nanowire Networks," *Nano Letters*, vol. 18, pp. 2666–2671, Apr. 2018.
- [443] M. Friedl, K. Cervený, C. Huang, D. Dede, M. Samani, M. O. Hill, N. Morgan, W. Kim, L. Güniat, J. Segura-Ruiz, L. J. Lauhon, D. M. Zumbühl, and A. Fontcuberta i Morral, "Remote Doping of Scalable Nanowire Branches," *Nano Letters*, vol. 20, pp. 3577–3584, May 2020. Publisher: American Chemical Society.
- [444] B. P. Gorman, D. Diercks, N. Salmon, E. Stach, G. Amador, and C. Hartfield, "Hardware and Techniques for Cross- Correlative TEM and Atom Probe Analysis," *Microscopy Today*, vol. 16, pp. 42–47, July 2008.
- [445] D. Diercks, B. P. Gorman, C. L. Cheung, and G. Wang, "Techniques for Consecutive TEM and Atom Probe Tomography Analysis of Nanowires," *Microscopy and Microanalysis*, vol. 15, pp. 254–255, July 2009.
- [446] J. Qu, D. Wong, S. Du, L. Yang, S. Ringer, and R. Zheng, "Methodology exploration of specimen preparation for atom probe tomography from nanowires," *Ultramicroscopy*, vol. 159, pp. 427–431, Dec. 2015.
- [447] S. Koelling, A. Li, A. Cavalli, S. Assali, D. Car, S. Gazibegovic, E. P. A. M. Bakkers, and P. M. Koenraad, "Atom-by-Atom Analysis of Semiconductor Nanowires with Parts Per Million Sensitivity," *Nano Letters*, vol. 17, pp. 599–605, Feb. 2017.
- [448] J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon, "High-resolution detection of Au catalyst atoms in Si nanowires," *Nature Nanotechnology*, vol. 3, pp. 168–173, Mar. 2008.
- [449] Y. Yasuda, S. Koh, K. Ikeda, and H. Kawaguchi, "Crystal growth of InGaAs/InAlAs quantum wells on InP(110) by MBE," *Journal of Crystal Growth*, vol. 364, pp. 95–100, Feb. 2013.
- [450] R. H. Dixon and P. J. Goodhew, "On the origin of misfit dislocations in InGaAs/GaAs strained layers," *Journal of Applied Physics*, vol. 68, pp. 3163–3168, Oct. 1990.
- [451] R. France, A. J. Ptak, C.-S. Jiang, and S. P. Ahrenkiel, "Control of asymmetric strain relaxation in InGaAs grown by molecular-beam epitaxy," *Journal of Applied Physics*, vol. 107, p. 103530, May 2010.
- [452] X. Zhang and D. W. Pashley, "A comparison of strain relief behaviour of In_xGa_{1-x}As alloy on GaAs (001) and (110) substrates," p. 7.

- [453] X. Zhang, D. W. Pashley, J. H. Neave, L. Hart, and B. A. Joyce, "The strain relaxation of $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}$ on GaAs (110) grown by molecular beam epitaxy," *Journal of Applied Physics*, vol. 78, pp. 6454–6457, Dec. 1995.

APPENDIX A

Nanowire Manipulation and Isolation for Atom Probe and Synchrotron Studies

This appendix reviews nanowire manipulation techniques used in this thesis, including pick-up of dispersed nanowires, direct pick-and-place of nanowires, and nanowire isolation on substrate for X-ray studies.

Nanowire pick-up refers to the welding of a single nanowire directly onto a tungsten micromanipulator tip for use in atom probe tomography, enabling the nanowire to be removed from a surface. The procedure for this technique is summarized in Figure A.1. First a transmission electron microscopy (TEM) grid is cut in half using a clean razor blade. In this work, 1000 mesh Cu TEM grids are used. Then the individual grid halves are picked on their edge using a piece of Cu tape, with the smooth side of the TEM grid facing upward. The tape/grid are attached to an SEM stub, with the TEM grid protruding beyond the edge of the stub (as seen in A.1(a)). Care must be taken to prevent bending of the fragile TEM grids. Second, holding the SEM stub upside down, the top of the TEM grids are gently scraped across the surface of the nanowire array, such that nanowires are transferred to the edge of the TEM grid (A.1(b)). Optical imaging can be used to estimate the density of nanowires transferred onto the grid. Third, the grids are imaged using SEM, noting the location of ideal nanowire candidates. A good nanowire candidate for pick up is one sticking at least halfway off the end of the grid and sufficiently isolated from other wires, as in A.1(d). Last, the SEM stub is transferred into a FIB/SEM dual beam system that includes a piezo-manipulator that can mount detachable tungsten microtips. In this work, a Kleindiek Nanotechnik piezo-manipulator (a few nanometer precision) was used. A Micromanipulator 7X Tungsten (W) Cat Whisker Fine Probe Tip (100 nm diameter at the apex) is attached to the manipulator arm. These tips are removable, and thus can be directly inserted into the atom probe (after cutting their

length down, crimping them into a copper sample stub, and screwing them into a LEAP puck). In the FIB/SEM, a flat is milled in the W tip apex (parallel with the tip axis), aligned with the nanowire of interest, brought into contact with the nanowire from below, and electron-beam (e-beam) welded with a Pt gas injection source. The vacuum chamber is vented, the tip rotated 30 degrees, and another e-beam Pt weld is made at the other side of the nanowire/tip contact. This method is generally successful if the nanowire sticks out at least 1-2 μm after the edge of the W tip, thus nanowires of $< 1 \mu\text{m}$ total length cannot be prepared in this way. A final tip prepared for atom probe is seen in A.1(e). In most cases, nanowires are aligned parallel to the W tip, as seen in this example, but in some cases, nanowires are intentionally angled ($20\text{-}40^\circ$) to produce an asymmetric atom probe analysis for viewing the tip surface. A number of variations of this pick-up method are discussed in the literature [444, 445, 446].

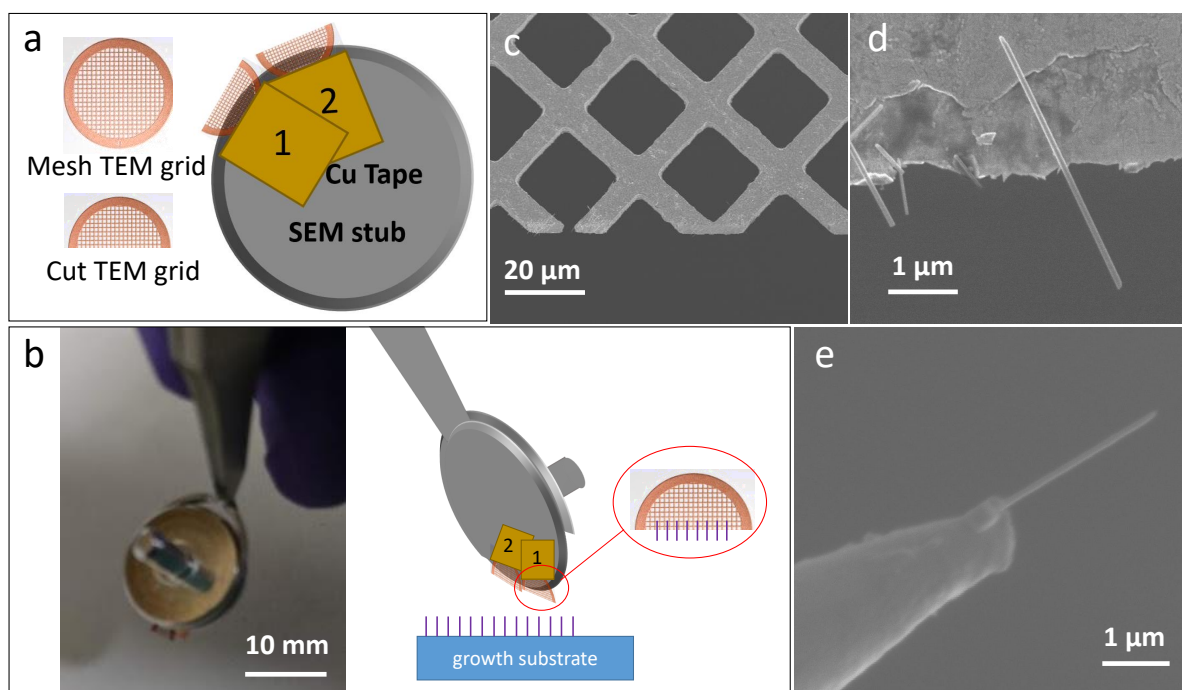


Figure A.1. Pick-up of nanowires for atom probe tomography. (a) A Cu mesh TEM grid is cut in half and taped to the edge of an SEM stub. (b) The TEM grids are gently brought into contact with the nanowire array. (c) The nanowires protrude from the edge of the TEM grid. (d) Nanowires that are hanging at least halfway off the grid should be selected for pick up. (e) Nanowires are Pt glued to a W micromanipulator tip for APT analysis.

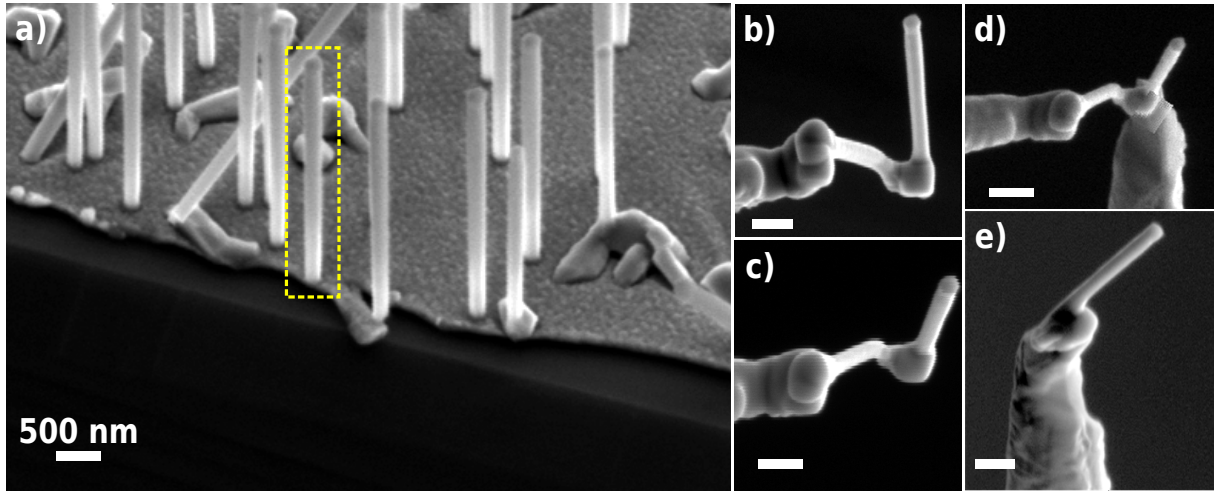


Figure A.2. Direct pick-and-place of nanowires for correlative APT. (a) A specific nanowire is picked out on the edge of a cleaved substrate, such as one that has been characterized previously with a non-destructive technique. (b) The vertical nanowire is welded to a sacrificial nanowire on a W tip and is pulled off the substrate. (c) The manipulator is manually rotated and (d) brought into contact with the micropost. (d) After welding and removing the sacrificial nanowire, the nanowire of interest is left welded to the micropost at a high tilt angle in this example to access the nanowire surface during APT measurements. For symmetric APT measurements, the nanowire should be welded vertically.

An alternative method for nanowire isolation for APT measurements is direct pick-and-place. This method can be used when isolation of a specific nanowire is desired (as needed for correlative measurements). The nanowire array must be cleaved such that vertical nanowires stand within 1 μm of the substrate edge. Care should be taken during substrate handling and transport, as electrostatic discharge can cause nanowires on the very edge of the substrate to break off (this is not generally a concern for nanowire arrays). In this method, a sacrificial nanowire is welded to the W manipulator using the nanowire pick-up procedure. This nanowire does not need to be the same material as the nanowire of interest, but should ideally be $>3 \mu\text{m}$ long. It is also important that the sacrificial nanowire have a larger tensile strength than shear strength so that it will not break when the nanowire of interest is pulled off the substrate, but will break when sheared in the final step. GaAs is used in this work, but InP has also been shown to meet this requirement 447. In some cases nanowires are knocked over from cleaving the substrate of interest; if they are hanging off the edge of the substrate and meet the previous requirements,

they can also be used as a sacrificial wire. Next, using the Kleindiek piezo-manipulator the sacrificial nanowire is brought into contact with the base of the nanowire of interest on the right side (as seen by Figure A.2). The sacrificial nanowire should not bend the vertical nanowire and the sacrificial wire should not touch the substrate (if they are in contact the Pt deposition may attach the sacrificial wire to the substrate surface). A Pt e-beam weld is made at the top interface of the sacrificial wire and vertical wire contact. Using a gentle horizontal force, the vertical nanowire is then pulled off the surface, as seen in A.2(b). Occasionally an asymmetric field of view is desired in APT. This is needed if investigating the nanowire surface or when asymmetrically probing nanowire shells (as in Section 5.1). In this case the nanowire can be mounted at an angle by venting the SEM/FIB chamber and manually rotating the W manipulator by 20-40°. If no angle is desired, this step is skipped. The vertical nanowire is then brought into contact with the milled face of a Si micropost or a vertically mounted W tip, and a Pt e-beam weld is made at the base of the nanowire. Finally, the W tip is slowly moved back and forth horizontally until the sacrificial nanowire breaks off, either at the tip of the manipulator or the base of the mounted nanowire (as shown in A.2(e)). If the sacrificial nanowire breaks off at the manipulator tip, remaining on the Si micropost, it should be coated in a thin layer of Pt to prevent evaporation during APT measurements. More details on the process can be found in reference 447.

Finally, nanowires also need to be isolated for synchrotron measurements to prevent simultaneous overlapping diffraction peaks from multiple wires. The following procedure was used to isolate nanowires for ptychography and nanodiffraction experiments. Specially designed nanowire substrates were obtained from NORCADA Inc. An overview of these substrates is given in Figure A.3(a): a 10 μm thick Si film is attached to a 3.5 mm $\times$ 1.5 mm Si substrate (300 μm thick) such that the film extends 300 nm off the long end of the substrate. This thin Si “diving-board” is transparent to high energy X-rays. Cr or Pt fiducial markers were fabricated onto the diving-board as outlined in A.3(a). Nanowires are then dropcast onto the diving-board. Alternatively, nanowires that have been dry-transferred to a half TEM grid (as outlined in Figure A.2) can be subsequently transferred to the diving-board by gently scraping the TEM grid across the diving-board face.

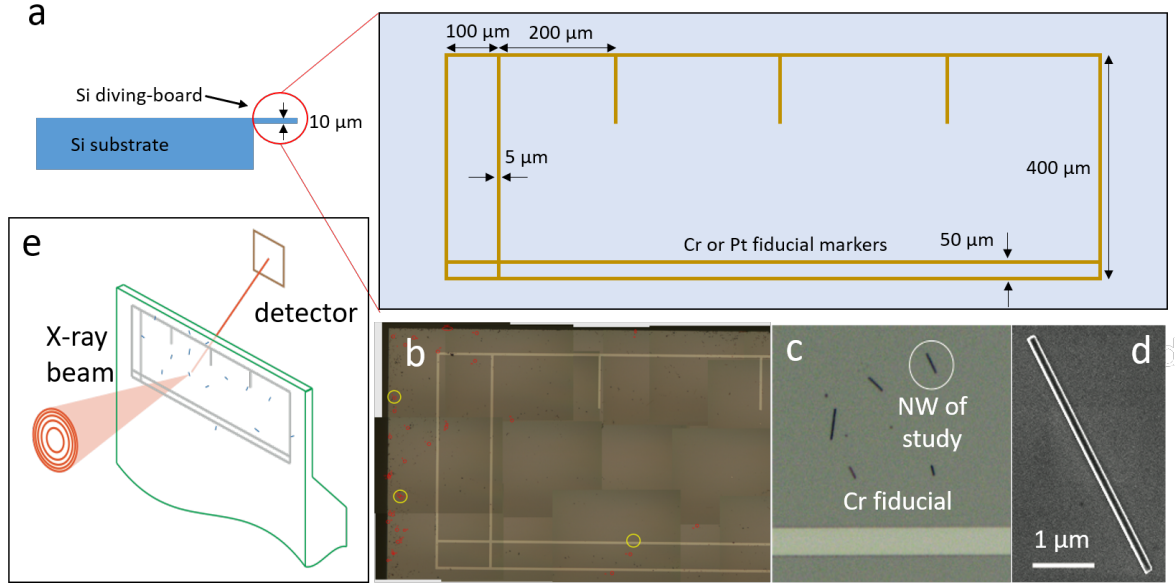


Figure A.3. Overview of nanowire transfer to Si diving-boards for synchrotron measurements. (a) Schematic of Si diving-board and overview of Cr or Pt fiducial markers fabricated on the diving-board. (b) Stitched map of optical images outlining the location of the nanowires with respect to metal fiducials. (c) Magnified optical image where single nanowires or nanowire bunches can be located. (d) SEM image of nanowire circled in (c). (e) Coarse schematic of beamline setup, where focused synchrotron X-rays can penetrate the 10 μm diving board such that diffraction from the nanowires can be collected on the detector.

In order to locate nanowires during synchrotron measurements, optical images of the diving-board should be collected and stitched together as in A.3(b,c). This map can be used to locate nanowires in SEM and at the beamline with respect to the metal fiducials. From the optical images, nanowires are identified at very low resolution, so SEM is performed to confirm that nanowires are fully isolated (not multiple wires) and fixed to the substrate on a single facet (not tilted), as in A.3(d). The thin coating of carbon deposited during SEM imaging helps adhere the nanowires to the diving-board. Nanowires that are not imaged may move around on the diving-board once exposed to the X-ray probe. Alternatively, a thin carbon coating can be applied before synchrotron measurements. At the beamline, nanowires of interest from SEM are traced back to their location with respect to Cr fiducials by using the stitched

optical image. Then X-ray fluorescence is used to locate the Cr fiducials and subsequently the nanowire of interest.

APPENDIX B

Measuring Accurate Dopant Concentrations via Atom Probe Tomography

In Chapter 3, the correlation between chemical and electrical dopants in InAs nanowires, was reported based on atom probe tomography analysis of chemical doping. The identification and quantification of dilute species may require analysis beyond that needed for more abundant species. This appendix describes in more detail the approaches used to accurately determine local Si dopant concentrations in InAs nanowires described in Chapter 3.

B.1. Measuring Dilute Si Dopants in InAs Nanowires

While APT has the potential for part-per-million (ppm) chemical sensitivity, noise sources can limit detection of dilute species even at levels greater than 100 ppm. Noise from uncorrelated evaporation can be readily reduced by tuning APT parameters such as laser energy, based temperature, and pulse frequency. However, optimizing conditions to minimize background counts will not always produce the highest quality APT reconstruction [422]. For example, if laser energy is increased, the standing voltage will decrease, producing a reduction in uncorrelated evaporation events, lowering the background level. However, if the laser energy is too high, tip heating can cause ions to migrate on the tip surface and evaporate as complex species. This will reduce the spatial accuracy of the reconstruction. The peaks of majority species or dilute species, including surface impurities, can also overlap with dopant peaks, complicating the calculation of dopant concentrations, as described in Section B.2. A higher tip temperature can also induce a higher background level due to uncorrelated thermally-assisted field evaporation. At lower laser pulse frequency, there is more time between pulses for the tip to cool down. Therefore, if a higher laser energy is needed for the measurement of dilute species, a lower laser pulse frequency can be used to

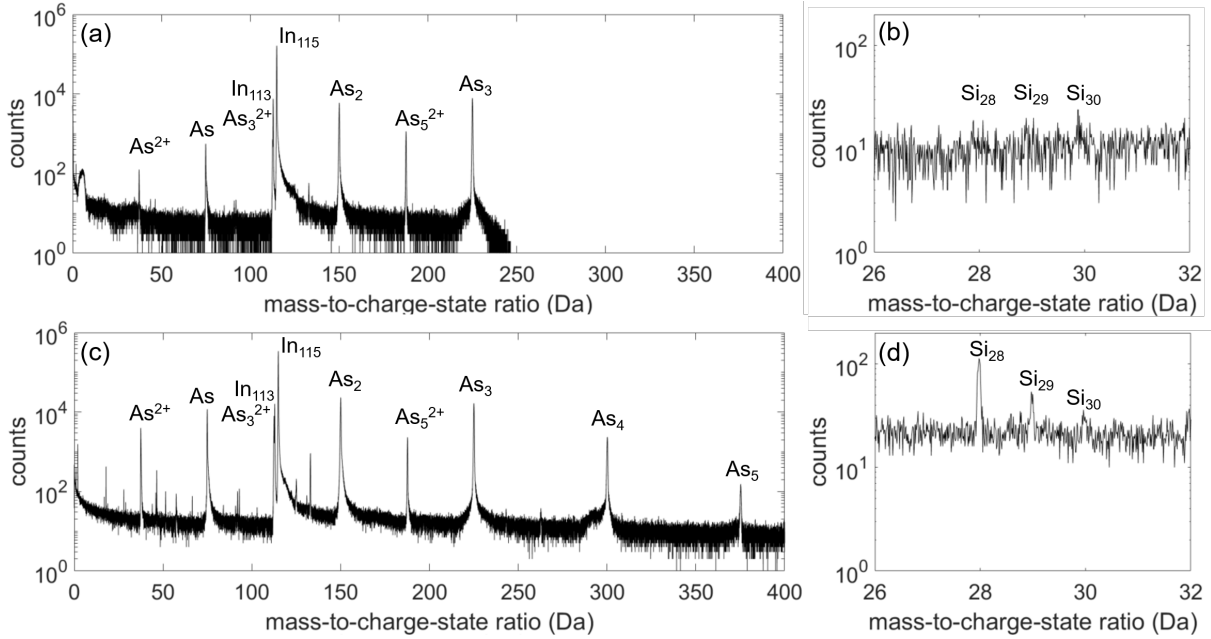


Figure B.1. Change in mass spectrum noise by modifying laser pulse frequency. (a) Mass spectra for InAs at the low doping condition (11 A) at a laser pulse frequency of 500 kHz. (b) Magnified mass spectra from (a) between 26-32 Da. Si peaks expected in this region are not visible. (c) Mass spectra for a separate run of InAs at the low doping condition (11 A) at a laser pulse frequency of 250 kHz (d) Magnified mass spectra from (c) between 26-32 Da. Si peaks at 28, 29, and 30 Da are visible at these conditions. Lowering the laser pulse frequency was found to reduce the background level and allow for the detection of dilute Si species ($\sim 5 \times 10^{18} \text{ cm}^{-3}$).

reduce tip heating. Further, if the laser pulse rate is too high heavier species may not make it to the detector before another laser pulse is initiated. If this happens, the mass-to-charge ratio of these ions will be mislabeled. Note that if the standing voltage is too high, additional uncorrelated evaporation will occur between pulses.

The effect of pulse frequency on Si dopant detection in InAs nanowires is seen in Figure B.1. Figure B.1(a) and c show mass spectra taken from a cylindrical ROI in the center of APT reconstructions for InAs nanowires at the lowest doping condition (11 A), as described in Chapter 3. Additionally, the spectra are magnified around the Si peaks from 26-32 Da in B.1(b) and d. The measured spectra were collected at the following APT conditions: 30 K, 0.2 pJ laser energy, and 0.5% detection rate. However, the spectra were taken at different laser pulse frequencies, 500 kHz for B.1(a,b) and 250 kHz for B.1(c,d).

In the higher pulse rate spectra (500 kHz), only ions with mass-to-charge ratios up to 250 Da are collected, as compared to 600 Da for the 250 kHz spectra (cut off in plot at 400 Da for clarity). Comparing the magnified spectra in B.1(b) and (d), which are plotted on the same scale, it is evident that the background level in (b) is larger than that in (d). Additionally in B.1(d), Si peaks are clearly resolved at 28, 29, and 30 Da. In B.1(b), no Si peaks are resolved at 28 and 29 Da. A small peak is visible at 30 Da, but given the relatively low percentage of Si that exists as the Si_{30} isotope, this peak is not expected to be due to Si. The reduction in laser pulse frequency reduced the overall background in the data, resulting in the detection of Si dopants at concentrations of $\sim 5 \times 10^{18} \text{ cm}^{-3}$.

Even if the background level is too high to resolve dopant peaks, as in Figure B.1(b), some information about the dopant concentration can still be extracted. An upper bound of the Si concentration can be calculated by determine the root-mean-squared (RMS) fluctuations in the background on each side of the Si peak. For the spectrum shown in B.1(b), the RMS fluctuations are calculated to be $\sim 7 \times 10^{18} \text{ cm}^{-3}$, which can be treated as an upper bound for the Si dopant concentration. This is consistent with the measurement in B.1(d), which has a Si concentration of $\sim 5 \times 10^{18} \text{ cm}^{-3}$, a value that falls beneath the RMS background fluctuations in B.1(b). More details on this calculation can be found in the supplemental material of reference 448.

B.2. Variable Laser Energy Studies

In addition to modifying laser pulse rate during APT measurements, the quantification of Si dopants in the InAs nanowires from Chapter 3 required the investigation of different laser pulse energies, as described in this section. In Figure B.1(d) three Si peaks are seen at 28, 29, and 30. However, the ratio of these peaks differs significantly from the ratios expected for Si isotopes: 92.22% Si_{28} , 4.69% Si_{29} , and 3.09% Si_{30} . This suggests that other ions or molecular species are present within the Si_{29} and Si_{30} range, such as COH (29), AsC^{3+} (29), and AsO^{3+} (30.3). Therefore, peaks at 29 and 30 are not included in calculations of Si concentration, and Si_{29} and Si_{30} is assumed to provide additional counts according to the natural abundance of isotopes. In addition, Si_{28}^{2+} , SiO, and SiAs are included in the calculation. The contribution of oxygen (in the form of CO (28)) must also be ruled out to calculate an accurate

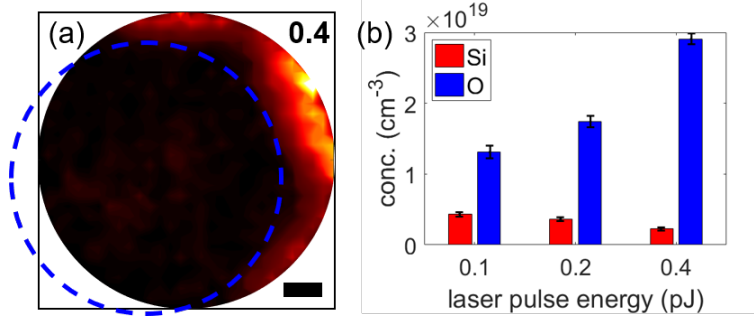


Figure B.2. Variations in APT concentration with laser pulse energy in InAs nanowire (13A). (a) Example of cylindrical ROI taken in the interior of the nanowire to determine the bulk Si concentration. (b) Measured concentration of Si (red) and oxygen (blue) for varying laser pulse energy. Higher laser energy leads to diffusion of oxygen from the surface during APT evaporation, therefore higher oxygen concentration. Si concentration shows smaller dependence on laser energy.

Si concentration. Since the nanowires were grown by MBE in a UHV system, measurable oxygen in the core of the nanowire is unlikely, but a thin surface oxide is expected due to environmental exposure post-growth. The laser pulsing could induce the diffusion of surface species into the tip region projected on the detector. To probe the possible contribution of surface oxide species, variable pulse energy APT measurements were performed.

During evaporation of a nanowire with high nominal doping (13 A), the laser energy was varied between 0.1 and 0.4 pJ. Oxygen and Si concentrations were extracted at each laser energy from a cylindrical ROI in the interior of the wire (where O species density was lower than $0.1 \text{ \#}/\text{nm}^3$).

The oxygen peaks included were O, O^{2+} , O_2 , OH, H_2O , H_2OAs , H_2OAs_2 , H_2OAs_3 , H_2OIn , $\text{H}_2\text{OIn}^{2+}$, InO , SiO , AsO , SiOH , InOH , and InOH^{2+} . The Si peaks included were Si_{28} , Si_{28}^{2+} , SiO , and SiAs . The interior portion of the nanowire contour for the 0.4 pJ condition is outlined in blue in B.2(a). The concentration of oxygen and of Si is shown as a function of laser energy in B.2(b). Oxygen increases significantly with increasing laser energy, suggesting that diffusion is occurring on the APT tip at higher energies. Si on the other hand does not change considerably with increasing laser power. This suggests that the increase in diffusion does not lead to CO (28) contributions to the Si_{28} peak.

The Si concentration cited in Chapter 3 are taken from APT runs with laser energies of 0.1 pJ to reduce surface diffusion. However, the higher laser energy runs are useful for investigating the surface

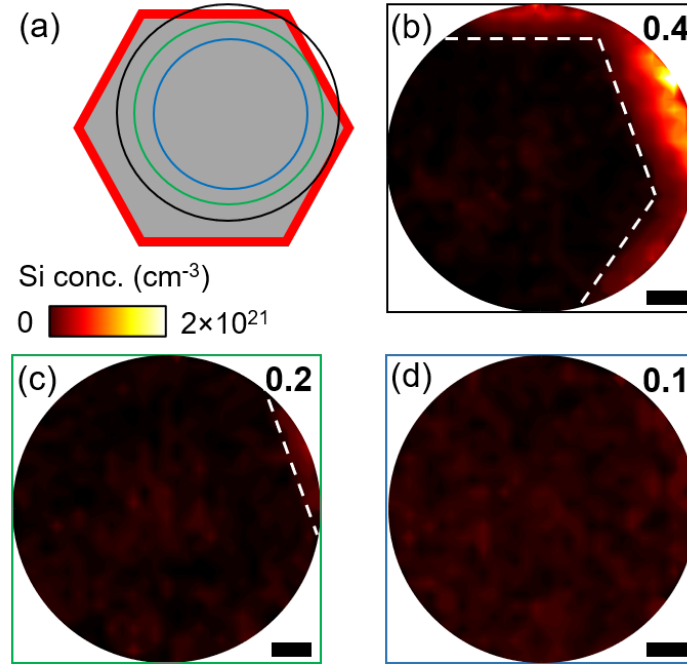


Figure B.3. Decreased field of view with lower laser pulse energy. Schematic of nanowire (grey) with Si (red) concentrated near the surface. Estimated field of view for each laser energy: 0.4 pJ (black), 0.2 pJ (green), 0.1 pJ (blue). 2D APT contour plots of Si concentration in highly doped InAs nanowire for 0.4 pJ (b), 0.2 pJ (c), and 0.1 pJ (d). All scale bars are 10 nm.

of the nanowires. This is demonstrated in Figure B.3. At increasing laser energies, the field of view in the APT reconstruction increases, revealing the presence of Si dopants on the surface of the nanowire at 0.4 pJ. This field of view change is due to the blunting of tip curvature at higher laser energy.

APPENDIX C

Effects of Beam Defocus on Nanodiffraction Analysis

Nano-focused X-ray diffraction is typically performed on thin films or bulk substrates. [241, 243, 355] In such cases, the sample is much larger than the probe size, and thus the object can be assumed to be of homogeneous tilt and thickness at a single probe position. However, in the case of nano-diffraction of individual nanowires, the probe size and nanowire diameter are of similar scale, and the effects of the thickness and nanowire faceting must be considered.

For example, in the nano-diffraction experiment from Chapter 5.1, a probe size of ~ 25 nm was used to measure a nanowire with diameter ~ 100 nm. Two-dimensional maps were taken, recording the 2θ position of the diffraction at each position, which can then be converted to a relative strain map as

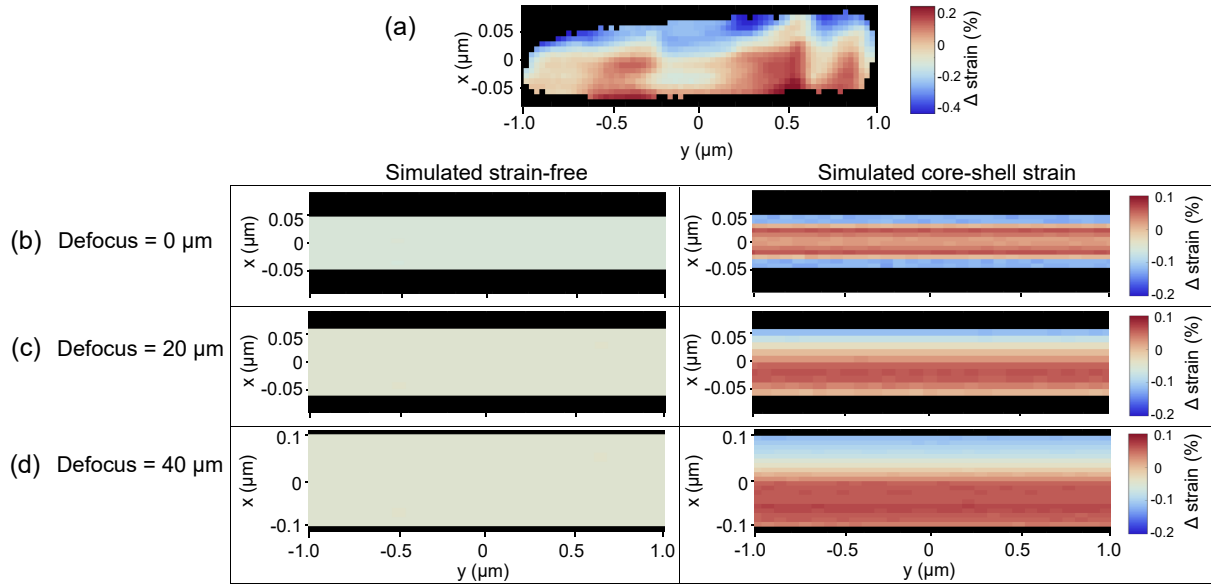


Figure C.1. Effect of defocus on nanodiffraction. (a) Relative strain field for the $\langle 110 \rangle$ scattering condition is shown for an example nanowire. Simulated strain field for strain-free nanowire (left) and core-shell nanowire (right) at (b) exact focus, (c) 20 μm defocus, and (d) 40 μm defocus.

described in Chapter 5.1. The relative strain field for the $\langle 110 \rangle$ scattering condition is shown for an example nanowire in C.1(a). The experimental data reveal a gradually increasing strain ramp across the nanowire diameter. Given that these nanowires are symmetric across the diameter, this radial variation is unexpected. However, since the edges of the nanowire have different faceting and thickness than the center of the wire, it is possible that the radially varying strain field is an artifact resulting from the nanowire shape; for example due to differences in X-ray absorption or beam deviations off the angled corner facets of the nanowire. To test this hypothesis, the strain field from a strain-free and core-shell GaAs/InGaAs nanowire (with 15% In) were simulated, as shown in Fig. C.1(b) (left and right respectively). A defocused X-ray probe and the shape alone do not reproduce the observed strain variation. However, an X-ray probe with a slight defocus of 20-40 μm produces radial variation in the core-shell nanowire that is similar to what is observed in the experiment, Figure C.1(c,d) (right).

To confirm that this radial variation was an effect of the X-ray probe defocus, a nanowire was measured at three focal conditions. For the same nanowire shown in Figure C.1(a), a lower resolution 2θ map is shown in Figure C.2. Here the perfect focal condition (0 μm) produces a relatively homogeneous nanowire, likely because spatial resolution is too low to resolve the strain field from the InGaAs shell. However, when defocusing the probe by just 20 μm , the radial variation reemerges.

The analysis above confirms that the variations along the nanowire length are not artifacts, and the variations across the diameter are not interpretable in terms of strain. For this reason, Chapter 5.1 shows lines scans from the center of the nanowire diameter. Considering that a single depth of focus for this probe is 10 μm , 20 μm is a relatively small defocus, but it creates a large variation in the apparent strain field. As such, this work shows that for X-ray nano-diffraction of 3D nanostructures, extra care must be taken to position the probe focus.

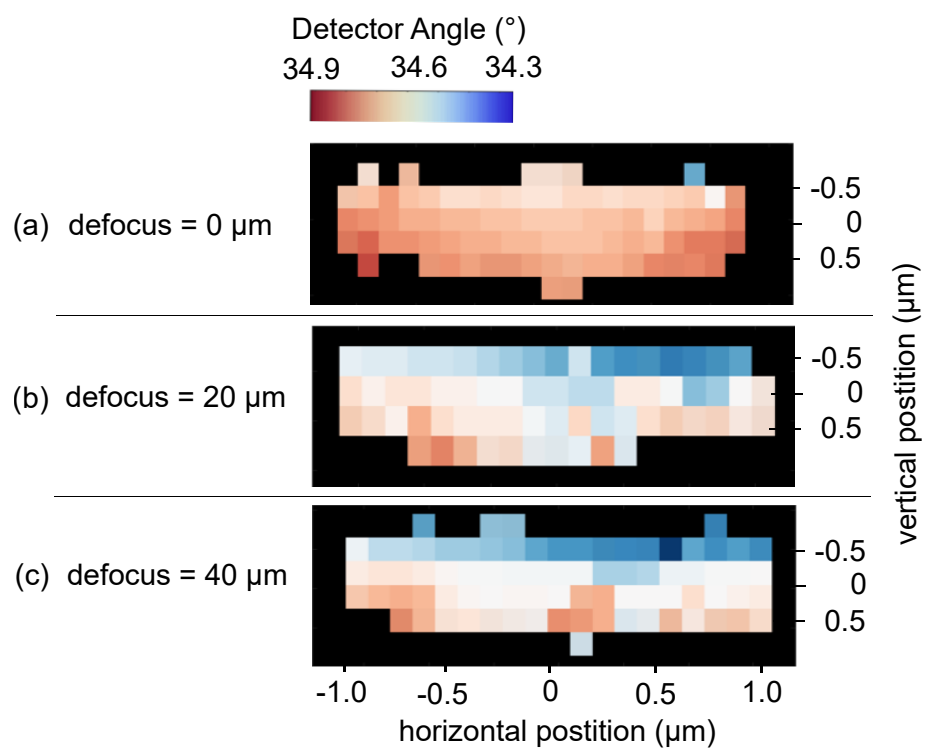


Figure C.2. 2θ map of same InGaAs QW nanowire shown in Figure C.1(a), at a lower resolution. Map shown for diffraction patterns taken (a) in focus, (b) at 20 μm defocus, and (c) at 40 μm defocus.

APPENDIX D

Misfit Dislocations in Asymmetric Quantum Well Nanowires

<https://www.overleaf.com/project/5e18ad358cad8c0001c7c5f6>

In section 5.2, the 3D lattice displacement in asymmetric core-shell nanowires was generated from coherent X-ray data. Deviations of this 3D displacement from displacement fields generated using FEM were attributed to the presence of interfacial dislocations; large isolated wraps in phase as seen in Figure D.1(a) indicate an abrupt change in lattice structure.

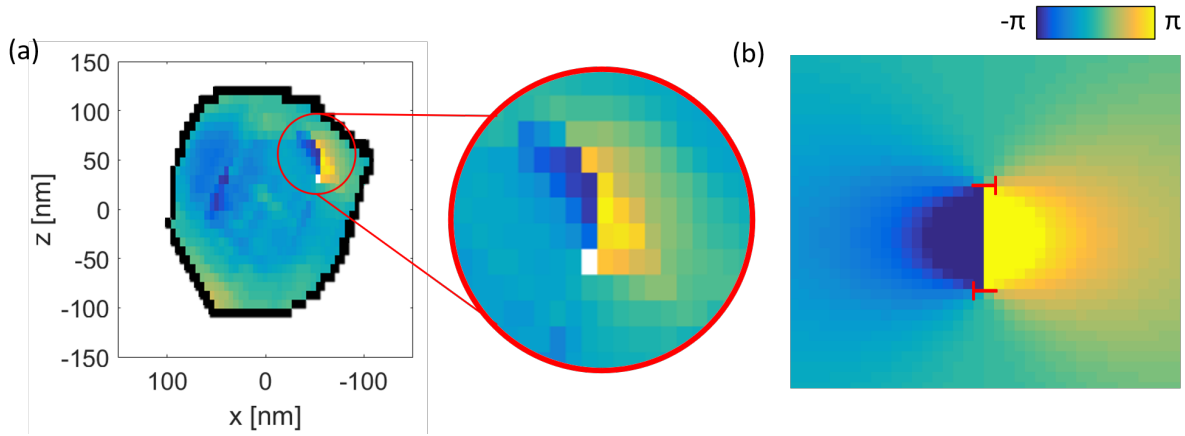


Figure D.1. (a) The $(11\bar{1})$ phase of NW-2, with the region around the 10 nm QW magnified. (b) 2D simulation of phase due to two opposite edge dislocations.

For example, a simulation of two antiparallel edge dislocations (D.1(b)) resembles the phase behavior observed in Figure D.1(a). The simulation was performed by calculating the displacement field associated with an individual edge dislocation given by:

$$(D.1) \quad U_x = \frac{b}{2\pi} \left[\tan^{-1} \left(\frac{y}{x} \right) + \frac{xy}{2(1-\nu)(x^2 + y^2)} \right]$$

$$(D.2) \quad U_y = \frac{b}{2\pi} \left[\frac{(-2\nu)}{4(1-\nu)} + \frac{xy}{2(1-\nu)(x^2 + y^2)} \right]$$

$$(D.3) \quad U_z = 0$$

Then the displacement along the $[11-1]$ direction was calculated as in the experimental data (i.e. $U_x + U_y - U_z$). The phase of this $[11-1]$ displacement is plotted in cross section in Figure D.1(b). For simplicity of simulation, these displacement fields are generated assuming the dislocation lines run down the $[111]$ nanowire growth axis and the Burgers vectors are perpendicular to the the dislocation line and the QW growth plane ($b=[110]$). While this is a useful example of the type of phase wrap that dislocations can produce, this simulation is not considered representative of the expected defect orientations of a zincblende crystal.

As discussed in Sections 5.2 and 2.5.3, there is not a consensus in literature on the critical thicknesses for defect formation in core-shell III-V nanowires, nor is it evident what type of dislocation will form in a given core-shell system. Both edge dislocation loops around the core or linear edge dislocations down the length of the nanowire have been predicted [275, 274]. Given the limited literature for misfit dislocations in core-shell III-V nanowires, probable defect structures can instead be generated from the literature on defect formation at the interface of bulk (110)-GaAs and InGaAs QWs (or other ZB III-V's) [449, 450, 451, 452, 453]. The most favorable defects at this interface are $[b][u]$: (1) $\frac{a}{2}\langle 011 \rangle [1\bar{1}0]$, (2) $\frac{a}{2}\langle 011 \rangle [1\bar{1}2]$, (3) $\frac{a}{2}\langle 01\bar{1} \rangle [1\bar{1}2]$, and (4) $\frac{a}{6}[112][1\bar{1}0]$, where b is the Burgers vector and u is the direction of the dislocation line. Defect type (4) is a Shockley partial dislocation, where two partial dislocations form with a stacking defect between them. Dislocation types (3) and (4) are most likely to form in larger quantum wells (>150 nm). It is therefore most likely that $\frac{a}{2}\langle 011 \rangle [1\bar{1}0]$ dislocations or $\frac{a}{2}\langle 011 \rangle [1\bar{1}2]$ Shockley partial dislocations will form to relieve strain at the interface of GaAs and InGaAs QWs. [453] There are additional defect structures of higher energy predicted for (110)-GaAs and InGaAs interfaces which are unlikely in planar QWs. However, these energies have not been calculated for the nanowire geometry, so other dislocation geometries are not completely ruled out. While CDI does allow for observation of strain and structure in the asymmetric QW nanowires, it does not provide an atomic resolution view of the defects, meaning the identity of the dislocations cannot be directly resolved in general. Further, given that multiple types of dislocation geometries (with any number of dislocations) are possible, it is

challenging to determine the dislocation structure that will produce a displacement field that matches the measured 3D reconstructions. As such, electron microscopy is needed to fully characterize the defect structure in these nanowires.