

UC San Diego

UC San Diego Electronic Theses and Dissertations

Title

Toward nanowire devices and systems : heterostructure design and dielectrophoretic integration

Permalink

<https://escholarship.org/uc/item/9mj8c88v>

Author

Raychaudhuri, Sourobh

Publication Date

2009

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA, SAN DIEGO

**Toward Nanowire Devices and Systems:
Heterostructure Design and Dielectrophoretic Integration**

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Electrical Engineering (Applied Physics)

by

Sourobh Raychaudhuri

Committee in Charge

Professor Edward T. Yu, Chair
Professor Peter M. Asbeck
Professor Prabhakar R. Bandaru
Professor S. S. Lau
Professor Jan B. Talbot

2009

Copyright

Sourobh Raychaudhuri, 2009

All rights reserved

The Dissertation of Surobh Raychaudhuri is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2009

To my family.

TABLE OF CONTENTS

Signature Page	iii
Dedication	iv
Table of Contents	v
List of Figures	viii
List of Tables	xiv
Acknowledgments	xv
Vita	xviii
Abstract of the Dissertation	xx
Chapter 1 Introduction	1
1.1 Semiconductor Nanowires	1
1.2 Semiconductor Nanowire Fabrication	3
1.2.1 VLS Growth Mechanism	4
1.2.2 Nanowire Heterostructures	6
1.3 Nanowire Devices and Applications	8
1.4 Nanowire Integration	11
1.4.1 Fluidic Assembly	13
1.4.2 Langmuir-Blodgett Technique	14
1.4.3 Template Based Assembly	16
1.4.4 Dielectrophoretic Assembly	18

Chapter 2	Critical Dimensions in Coaxial Nanowire Heterostructures. . . .	25
2.1	Introduction.	25
2.2	Analytical Framework.	29
2.2.1	Coherent Strain Energy Calculation.	32
2.2.1.1	Strain Energy in Wurtzite Nanowires	36
2.2.1.2	Strain Energy in Zinc Blende Nanowires	43
2.2.2	Partial Relaxation Through Dislocation Formation.	46
2.2.2.1	Relaxation in Wurtzite Nanowires	46
2.2.2.2	Relaxation in Zinc Blende Nanowires.	50
2.2.3	Critical Geometry Calculation.	53
2.3	Results and Discussion.	54
2.4	Conclusions.	62
Chapter 3	Dielectrophoretic Integration.	68
3.1	Introduction.	68
3.1.1	Dielectrophoresis.	69
3.1.2	DEP and nanowires.	76
3.2	Low Frequency DEP Manipulation.	81
3.2.1	Experimental Setup and Procedure	81
3.2.2	Experimental Results.	84
3.2.3	Analysis.	86
3.2.3.1	Electro-osmotic Fluid Flow.	86
3.2.4	Experimental Conclusions.	89

3.3	Precision DEP Alignment	89
3.3.1	Experimental Setup and Procedure	89
3.3.2	Experimental Results.	93
3.3.2.1	Post-Alignment Electrical Contact	93
3.3.2.2	Large Scale Nanowire Alignment.	94
3.4	Precision DEP Analysis.	97
3.4.1.	Effect of Signal Frequency	97
3.4.2.	Macroscopic Electrode Design	102
3.4.3	Discussion of Other Relevant Factors	105
3.5	Conclusions.	107
Appendix A	Polydimethylsiloxane (PDMS) Preparation.	113
Appendix B	DEP electrode Fabrication	115
B.1	Introduction.	115
B.2	Wafer Preparation	115
B.3	Alignment Site Patterning and Metal Deposition	116
B.4	Probe Pad Patterning and Metal Deposition	118
B.5	Passivation Layer Fabrication.	120
Appendix C	Alignment Site Modeling Using COMSOL.	122

LIST OF FIGURES

Figure 1.1	2
Scaling of transistor size (physical gate length) with technology node to sustain Moore's Law. Nodes with feature size less than 100 nm can be referred to as nanotechnology. By 2011, the gate length is expected to be at or below 10 nm. Transistor scaling will be enabled by integration of emerging nanotechnology options on to the Si platform [Ref. 5].	
Figure 1.2	4
Schematic of VLS growth of Si nanowires (SiNWs). A liquid alloy droplet AuSi is first formed above the eutectic temperature (363 °C) of Au and Si. The continued feeding of Si in the vapour phase into the liquid alloy causes oversaturation of the liquid alloy, resulting in nucleation and directional nanowire growth [Ref. 6].	
Figure 1.3	5
In situ TEM images recorded during the process of nanowire growth. (a) Au nanoclusters in solid state at 500 °C; (b) alloying initiates at 800 °C, at this stage Au exists in mostly solid state; (c) liquid Au/Ge alloy; (d) the nucleation of Ge nanocrystal on the alloy surface; (e) Ge nanocrystal elongates with further Ge condensation and eventually a wire forms...	
Figure 1.4	7
Nanowire heterostructure synthesis. (a) Preferential reactant incorporation at the catalyst (growth end) leads to one-dimensional axial growth. (b) A change in the reactant leads to either (c) axial heterostructure growth or (d) radial heterostructure growth depending on whether the reactant is preferentially incorporated (c) at the catalyst or (d) uniformly...	
Figure 1.5	13
Schematic of fluidic assembly. (A) A channel formed when the PDMS mold was brought in contact with a flat substrate. Nanowire assembly was carried out by flowing an nanowire suspension inside the channel with a controlled flow rate for set duration. Parallel arrays of nanowires are observed in the flow direction on the substrate when the PDMS mold is...	
Figure 1.6	15
Schematic of Langmuir-Blodgett technique. Nanowires (blue lines) in a monolayer of surfactant at the air-water interface are (a) compressed on a Langmuir-Blodgett trough to a specified pitch. (b) The aligned nanowires are transferred to the surface of a substrate to make a uniform parallel array. (c) Crossed nanowire structures are formed by uniform transfer...	
Figure 1.7	18
An example of patterned catalyst MOCVD grown nanowires on electrically isolated islands achieved through wafer bonding. (a) 85° and (b) 45° angle-view FE-SEM images of vertical and electrically isolated InAs nanowires on SiO ₂ /Si. (c) Zoom-in FE-SEM image of an InAs NW with an InAs island at its base, sitting on SiO ₂ substrate and electrically isolated for...	
Figure 2.1	26
Plot of energy bandgaps and lattice constants for various semiconductor materials and their alloys. Solid lines denote direct bandgaps and dotted lines denote indirect bandgaps. [Ref. 1].	

Figure 2.2	27
Schematic depictions of relaxed substrate material (top left) and relaxed epitaxial material (top right) with different lattice constants. In a coherently strained epitaxial layer (bottom left) the epitaxial film is forced to conform to the lattice constant of the substrate resulting in strain throughout the epitaxial layer. In a strain relaxed epitaxial layer the layer has gotten...	
Figure 2.3	30
Schematic diagram of core-shell nanowire heterostructure where r , h , and L represent the core radius value, the shell thickness value, and the length of the wire respectively. The nanowire is assumed to be oriented along the [0001] direction for wurtzite nanowires and the [111] direction for zinc blende nanowires	
Figure 2.4	33
Diagram of the orientation of stress (σ) and strain (ϵ) components in (a) planar heterostructures and (b) coaxial heterostructures.	
Figure 2.5	34
(a) Cutaway and (b) cross-sectionsl diagram of coaxial nanowire structure. $\{x, y, z\}$ denote the reference axes of the system while $\{x', y', z'\}$ denote the normal, tangential and longitudinal axes for a specific point on the circular interface corresponding to the angle ϕ .	
Figure 2.6	41
Plot of the (a) cross-sectional equilibrium lattice constants a and (b) longitudinal lattice constant c as functions of shell thickness. The structure considered is comprised of a 25 nm GaN core and an $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ shell. The maximum and minimum y axis values on both plots are set to be the relaxed core and shell lattice constants, respectively.	
Figure 2.7	47
(a) Orientation of an edge dislocation line along the axis of the wire with a Burgers vector, b_{line} , tangential to the circular heterointerface. (b) Orientation of an edge dislocation loop in the cross-sectional plane of the wire with Burgers vector, b_{loop} , along the length of the wire.	
Figure 2.8	51
(a) Stacking sequence of (111) planes in a coherently strained [111] zinc blende coaxial nanowire. (b) Stacking sequence of (111) planes in a [111] zinc blende nanowire with a stacking fault in the core region. The 'X' represents the location of an edge dislocation loop formed around the core as a result of the stacking error.	
Figure 2.9	55
Schematic plot of the critical dimensions for a (a) wurtzite and (b) zinc blende coaxial nanowire structure. The shaded region of the plots show all possible strained coherent geometries, which are quantified by the critical core radius r_{crit} and the critical shell thickness curve (thick red portion of the curves).	
Figure 2.10	57
Plot of the critical core radius for various nanowire heterostructures as a function of alloy composition. The structures considered are comprised of an InAs core with an $\text{In}_{1-x}\text{Ga}_x\text{As}$ shell (●), $\text{Si}_{1-x}\text{Ge}_x$ core with a Si shell (■), GaN core with an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ shell (▼), and $\text{In}_x\text{Ga}_{1-x}\text{N}$ core with a GaN shell (▲).	

Figure 2.11	59
Critical dimensions for various wurtzite nanowire heterojunctions comprised of (a) GaN cores with $\text{Al}_x\text{Ga}_{1-x}\text{N}$ shells and (b) $\text{In}_x\text{Ga}_{1-x}\text{N}$ core with GaN shells.	
Figure 2.12	60
Critical dimensions for various zinc blende nanowire heterojunctions comprised of (a) $\text{Si}_{1-x}\text{Ge}_x$ cores with Si shells and (b) InAs cores with $\text{In}_{1-x}\text{Ga}_x\text{As}$ shells.	
Figure 3.1	71
Schematic illustration of electrophoresis (a) and dielectrophoresis on a particle (b) and nanowire (c). Positive charge is represented in pink and negative charge is represented in blue. a) Electrostatic force on each charged particle will draw it toward the electrode of opposite polarity. b) A neutrally charged particle will form a dipole when placed in an external...	
Figure 3.2	73
Electrically neutral particle of radius R , permittivity ϵ_p and conductivity σ_p suspended in a medium of permittivity ϵ_m and conductivity σ_m in a uniform electric field of magnitude E_0 . [Ref. 37]	
Figure 3.3	77
SEM images [of DEP aligned carbon nanotubes] prepared at an electric field of 2.2×10^3 Vrms cm ⁻¹ with frequency of 10 Hz for (a) and (b), and 10 MHz (c) and (d); (a) and (c) were taken at the electrode's edge and (b) and (d) in the middle of gap between two electrodes [Ref 40].	
Figure 3.4	78
SEM photograph of assembly sites initially electrically isolated from the readout circuitry. [DEP] Assembled nanowires are clamped and connected to the readout circuit using a post-assembly e-beam lithography and metallization step [Ref. 59].	
Figure 3.5	80
The distribution of the yield rate for aligned GaN nanowires in the gap over the 200 electrode array with 10 V _{pp} at the frequencies of 10 kHz and 20 MHz [Ref. 60]	
Figure 3.6	81
SEM image of as grown InAs nanowires on an SiO ₂ substrate. The wires are approximately 60 nm in diameter and 20 μm in length before sonication. Scale bar is 10 μm .	
Figure 3.7	82
Commercially fabricated 5 x 5 electrode array with 100 μm diameter electrodes.	
Figure 3.8	83
Schematic diagram showing how de-ionized water solutions (a,c) and isopropyl alcohol solutions (b) wet the surface of the DEP chip. Because of the differing contact angles the distribution of nanowires above the electrode will be very different in the two cases. In order to perform a direct comparison a PDMS "cup" is used to contain the isopropyl alcohol ...	

Figure 3.9	85
SEM images of DEP electrodes after nanowire placement. Images are shown for nanowires suspended in de-ionized water and positioned using signal frequencies of 2 kHz (a) and 20 kHz (b) and nanowires suspended in isopropyl alcohol and positioned using signal frequencies of 2 kHz (c) and 20 kHz(d).	
Figure 3.10	87
Schematic illustration of electro-osmotic fluid motion. A charge layer of ions builds up at the fluid-electrode interface (shown in red). The electric field along the electrode (shown in purple) results in an electrostatic force which drags the charged layer along the surface of the electrode causing a fluidic motion, shown in green.	
Figure 3.11	90
SEM image of as grown InAs nanowires before suspension. Scale bar is 10 μm for figure, 200 nm for inset.	
Figure 3.12	91
Schematic diagram of electrode layer structure (top) and top-view of alignment site (bottom).	
Figure 3.13	92
SEM images of individual alignment sites after DEP alignment. SEM image of a precisely aligned nanowire taken at 45° (a), and from directly overhead (b). SEM image of an alignment site with both precise alignment and a stray nanowire (c). SEM image of an alignment site with just a stray wire (d). Scale bar is 5 μm for all images.	
Figure 3.14	94
IV curve of 4 aligned nanowires in parallel. Inset shows an SEM image of one such aligned wire after micro-fabrication has been carried out to remove oxide and deposit metal to make contact electrical contact with the alignment site. Scale bar for the inset is 5 μm .	
Figure 3.15	95
Optical microscope images of electrode arrays after DEP alignment. Precisely aligned sites are highlighted with a green box, stray wires are highlighted with red line. Each image is 500 x 500 μm .	
Figure 3.16	96
Histogram showing the percentage of alignment sites which attracted nanowires. Each bar is broken up to show the percentage of alignment sites which had only precisely aligned wires, both aligned and stray wires, and only stray wires. The histogram shows that with increasing frequency there is a decrease in the total number of wires collected but an increase in the ...	
Figure 3.17	99
Plot of the real part of the Clausius-Mossotti for the long and short axes of an InAs nanowire suspended in de-ionized water as a function of signal frequency.	

Figure 3.18	100
Diagram of a nanowire in an electric field pointing to the right with an arbitrary electric field gradient (top). DEP force angle and relative force magnitude are plotted as a function of gradient direction angle for signal frequencies of 10 kHz (diamonds), 1 MHz (triangles) and 10 MHz (circles).	
Figure 3.19	101
(a) and (b) both show finite element simulation results 5 μm above an alignment site. The white arrows represent the electric field direction (a) and electric field gradient direction (b). The coloring of both (a) and (b) represent the magnitude of the gradient vector squared (which corresponds to DEP force) on a linear scale where lighter shading indicate a greater...	
Figure 3.20	103
(a) shows optical microscope images of 5 alignment sites in both double and single bus bar architectures after DEP alignment. Circles indicate nanowire positions after alignment attempt. (b) shows the results of finite element simulations for the gradient of the electric field squared (which corresponds to DEP force) on a logarithmic scale where lighter...	
Figure C.1	123
COMSOL windows showing 3 dimensional view (left) and top view (right) of the double bus bar alignment site model with 50 μm spacing. Periodic boundary conditions are used to simulate the double bus bar effect.	
Figure C.2	123
COMSOL windows showing 3 dimensional view (left) and top view (right) of the single bus bar alignment site model with 50 μm spacing.	
Figure C.3	124
Alignment site model with SiN_x region highlighted (left) and SiN_x region parameter values (right).	
Figure C.4	124
Alignment site model with de-ionized water region highlighted (left) and de-ionized water region parameter values (right).	
Figure C.5	126
Alignment site model with electrode boundaries highlighted (left) and boundary parameter values for the positive electrode (right).	
Figure C.6	126
Alignment site model with upper and lower boundaries highlighted (left) along with their corresponding boundary parameter values (right).	
Figure C.7	127
Alignment site model with surrounding boundaries highlighted (left) along with their corresponding boundary parameter values (right).	

Figure C.8 127

Alignment site model with boundaries that are parallel to the double bus bars highlighted. These boundaries are set to be periodic to effectively model the double bus bar architecture.

Figure C.9 128

Alignment site model showing a 3 dimensional arrow plot of the electric field $5\ \mu\text{m}$ above an alignment site along with its corresponding plot parameter values (left).

Figure C.10 128

Alignment site model showing a slice plot along the y-z plane of the magnitude of the electric field, squared, on a log scale, $15\ \mu\text{m}$ away an alignment site along with its corresponding plot parameter values (left).

LIST OF TABLES

Table 2.1	61
Relevant physical parameters for wurtzite materials	

Table 2.2	61
Relevant physical parameters for zinc blende materials.	

ACKNOWLEDGEMENTS

I would first like to thank my advisor Prof. Edward T. Yu for his mentorship. Over the past several years his guidance and support have been instrumental in forming my abilities as a researcher. I have felt very fortunate to have a mentor who has not only been attentive and encouraging of my pursuits as a researcher but also of my development as a member of the university community.

I would like to acknowledge Prof. Peter Asbeck and Dr. S. S. Lau, not only for serving on my dissertation committee but also for providing me with advice and guidance in my early research endeavors. I would also like to acknowledge Prof. Prabhakar Bandaru and Prof. Jan Talbot for their participation on my committee. Their insightful comments played an important role in the development of this dissertation. I would also like to acknowledge Prof. Deli Wang whose lab has been an integral part of the nanowire effort at UCSD.

I would like to acknowledge Clint Novotny and Shadi Dayeh whose efforts have laid the groundwork for nanowire work at UCSD. In particular I would like to thank Shadi for providing the nanowires used in my experiments. I would also like to thank Jessica Godin, Jung Park and Arthur Zhang for their helpful discussions on optimizing and improving my device processing.

I would also like to thank our Nano3 Staff, Bernd Fruhberger, Ryan Anderson, Larry Grissom, Sean Parks and Maribel Montero. Through their efforts UCSD is able to operate and maintain a world-class clean room that has been essential to the completion of this dissertation.

Overall, my time in graduate school has been a very positive experience. This is in no small part due to the exceptional community, both in the Department of Electrical and Computer Engineering, as well as in the Jacobs School of Engineering. I would like to thank Karol Previte, Gennie Miranda, Rob Rome, Megan Scott and Bernadette Villaluz for helping to foster a sense of community within the department. I am grateful for the friendships that I have made and the support I have received while in graduate school. To make an inclusive list of persons to thank would be impossible, but in particular I would like to acknowledge Wayne Chen, Winnie Chen, Daniel Derkacs, Meredith Draa, Clay McPheeters, Smita Pathak, Peter Link and Hongtao Zhang.

Finally, I would like to thank my family for their love and support. My parents, Pranab and Ira Raychaudhuri, have always been encouraging of my pursuits. From an early age they fostered an environment that promoted exploration and curiosity, which has served me well as a researcher. My brother, Soumya Raychaudhuri, has always been a strong role model, mentor and friend, whose wisdom and advice has often helped me through some of the more challenging moments in my intellectual pursuits. My accomplishments are a result of the love, support and patience that my family has shown me and for this I cannot thank them enough.

Portions of chapter 2 have been published in Journal of Applied Physics, 2006, S. Raychaudhuri and E. T. Yu. The dissertation author is the first author of this paper.

Portions of this chapter 2 have been published in Journal of Vacuum Science and Technology B, 2006, S. Raychaudhuri and E. T. Yu. The dissertation author is the first author of this paper.

Portions of chapter 3 have been submitted for publication, 2009, S. Raychaudhuri, S. A. Dayeh, D. Wang and E. T. Yu. The dissertation author is the first author of this paper.

VITA

2002	B. S. Electrical Engineering, University of Illinois, Urbana-Champaign, IL
2005	M. S. Electrical Engineering, University of California, San Diego CA
2009	Ph. D. Electrical Engineering, University of California, San Diego CA

PUBLICATIONS

- **S. Raychaudhuri**, S. A. Dayeh, D. Wang and E. T. Yu, "Precise nanowire placement through dielectrophoresis" to be submitted (2009).
- **S. Raychaudhuri** and E. T. Yu, "Calculation of critical dimensions for wurtzite and cubic zincblende coaxial nanowire heterostructures," J. Vac. Sci. Technol. B 24, 2053 (2006).
- **S. Raychaudhuri** and E. T. Yu, "Critical dimensions in coherently strained coaxial nanowire heterostructures," J. Appl. Phys. 99, 114308 (2006).
- D. M. Keogh, J. C. Li, A. M. Conway, D. Qiao, **S. Raychaudhuri**, P. M. Asbeck, R. D. Dupuis, M. Feng, "Analysis of GaN HBT structures for high power, high efficiency microwave amplifiers," in High Performance Devices (Proceedings of the 2004 IEEE Lester Eastman Conference on High Performance Devices, Piscataway, NJ), p. 207-212 (2004).
- J. C. Li, D. M. Keogh, **S. Raychaudhuri**, A. Conway, D. Qiao, P. M. Asbeck, "Analysis of high DC current gain structures for GaN/InGaN/GaN HBTs." in High Performance Devices (Proceedings of the 2004 IEEE Lester Eastman Conference on High Performance Devices, Piscataway, NJ), p. 201-206 (2004)

- M. Feng, R. K. Price, R. Chan, T. Chung, R.D. Dupuis, D. M. Keogh, J. C. Li, A. Conway, D. Qiao, **S. Raychaudhuri**, P. M. Asbeck, “Current status of GaN heterojunction bipolar transistors.” in Proceedings of the 2004 Bipolar/BiCMOS Circuits and Technology Meeting, Piscataway, NJ, p. 26-31 (2004).
- R. B. Swint, V. C. Elarde, **S. Raychaudhuri**, J. J. Coleman, “Surface emitting lasers by selective area epitaxy for optical clock distribution,” Electron. Lett. 38, 794 - 795 (2002).
- R.B. Swint, T. S. Yeoh, V. C. Elarde, **S. Raychaudhuri**, M. S. Zediker, J. J. Coleman, “Curved and frustrated index guides for spatial mode control in high power diode lasers,” in Postdeadline Papers (Summaries of papers presented at the Conference on Lasers and Electro-Optics. Conference Edition, Washington, DC, USA), Opt. Soc. America. Part vol. 2, p. CPDB6-1-3 (2002).

ABSTRACT OF THE DISSERTATION

Toward Nanowire Devices and Systems: Heterostructure Design and Dielectrophoretic Integration

by

Sourobh Raychaudhuri

Doctor of Philosophy in Electrical Engineering (Applied Physics)

University of California, San Diego, 2009

Professor Edward T. Yu, Chair

Successes in the growth and fabrication of semiconductor nanowires, have led to new opportunities in device design for a wide variety of applications. Nanowires provide unique opportunities in device engineering in that their properties can be manipulated and tailored at the time of their creation to meet specific functional applications. Such nanowire devices can then be harvested to serve as building blocks for larger integrated systems. This is typically referred to as the “bottom-up” approach and adds a degree of flexibility not available in planner device fabrication.

In this dissertation we will examine a few specific aspects of semiconductor device and system engineering. Specifically we examine the geometric limits for coherence in radial nanowire heterostructures as well as the use of electric fields to align and place nanowires.

Novel nanowire device designs often require, or can benefit from, the use of heterostructures in their design. In determining the feasibility of these designs it is necessary to consider the strain that arises in heterostructures due to the lattice mismatch between materials. Such strain not only affects the electronic and optical properties of the device, but also determines the device dimensions at which coherence is lost and dislocations form, which will significantly alter or degrade device performance. In the second chapter of this dissertation we present a methodology to predict critical dimensions for coherently strained coaxial nanowire heterostructures based on a well-known formalism used to determine the critical thickness in planar epitaxial growth. It is anticipated that this model will serve as a guide to determine the feasibility of specific coherently strained nanowire heterostructure device designs.

While many individual nanowire devices and structures have been demonstrated, there are very few examples of large (or moderately sized) nanowire systems. Manipulating and placing nanowires in a useful fashion continues to be a considerable challenge. In the final chapter of this dissertation nanowire placement using Dielectrophoresis (DEP) is explored. DEP refers to the use of electric fields to manipulate neutrally charged particles in solution and can be used to attract nanowires (suspended in solution) onto predefined electrodes. DEP offers the ability to assemble

a wide variety of nanowires and is not limited by the way in which a nanowire is fabricated. Experimental results are presented and discussed demonstrating the feasibility of DEP as means to construct nanowire systems.

Chapter 1

Introduction

1.1 Semiconductor Nanowires

In his 1959 address to the American Physical Society, Richard Feynman pondered the challenges and limitations of miniaturization.¹ In his talk he submitted that it should be possible to fit the entire Encyclopedia Britannica on the head of a pin with room to spare. He went on to speculate on methodologies by which this could be accomplished, envisioning the ability to manufacture and manipulate on the molecular and atomic scale. While not actually using the term, Feynman's talk is often credited with introducing the concept of *nanotechnology*. Today nanotechnology refers to the manipulation of nanometer scale structures for specific applications.

Miniaturization has been of paramount importance to the semiconductor industry. For the past four decades Gordon Moore's famous prediction² that the number of transistors per unit area will double every two years has defined the industry. Continuing this trend with conventional fabrication techniques is becoming increasingly difficult. CMOS scaling is expected to reach 11 nm by 2022 with physical gate-lengths at around 5 nm.³ As shown in Figure 1.1, conventional scaling techniques are no longer sufficient to meet such demanding goals. As a result a

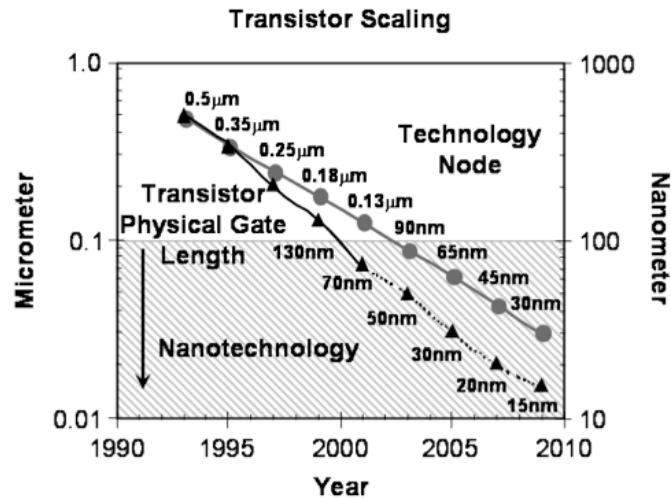


Figure 1.1

Scaling of transistor size (physical gate length) with technology node to sustain Moore's Law. Nodes with feature size less than 100 nm can be referred to as nanotechnology. By 2011, the gate length is expected to be at or below 10 nm. Transistor scaling will be enabled by integration of emerging nanotechnology options on to the Si platform [Ref. 5].

number of avenues of novel device research are being pursued including one-dimensional semiconductor structures⁴ known as nanowires. Semiconductor nanowires are cylindrical semiconductor structures with diameters of ~ 100 nanometers or less and can be microns in length. While semiconductor nanowires hold promise, much work still needs to be done to better understand and optimize these devices.⁵

Semiconductor nanowires provide a unique opportunity in that their properties, such as doping level or band-gap, can be manipulated and tailored at the time of their creation to meet specific functional applications.⁶ Such nanowire devices can then be harvested to serve as building blocks for larger integrated systems. This is typically referred to as the "bottom-up" approach and adds a degree of flexibility not available in planar device fabrication. With the "top-down" approach, typically used by the

semiconductor industry, structures are sculpted out of a single wafer using wafer-scale lithographic techniques to achieve functional devices, which will have physical parameters that are largely dictated by the properties of the starting wafer.

1.2 Semiconductor Nanowire Fabrication

Semiconductor nanowires have been fabricated using a variety of epitaxial growth techniques including metal-organic chemical vapor deposition (MOCVD),⁷⁻¹⁰ molecular (MBE)^{11,12} and chemical beam epitaxy (CBE)¹³, chemical vapor deposition (CVD),^{14,15} wafer annealing,¹⁶ and laser ablation.¹⁷⁻¹⁹ In MOCVD, gaseous metal-organics are flowed over a heated substrate at controlled pressures. The metal-organics break down providing metallic precursors for nanowire growth. MBE is carried out in ultra high vacuum where a beam of solid source material is directed at the substrate. CBE is also carried out in ultra high vacuum but in this case a beam of gaseous source material is directed at the substrate. CVD is performed by exposing the substrate to volatile precursors which react at the substrate. For wafer annealing, source material is provided by heating and thus decomposing the substrate wafer. In laser ablation, a laser is used to remove precursors from a solid source to achieve nanowire growth. In order to use these techniques to grow semiconductor nanowires the correct set of conditions must be employed. Typically a catalyst (often a metallic

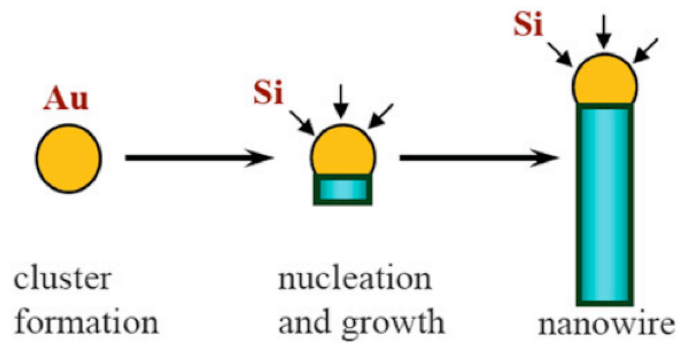


Figure 1.2

Schematic of VLS growth of Si nanowires (SiNWs). A liquid alloy droplet AuSi is first formed above the eutectic temperature (363 °C) of Au and Si. The continued feeding of Si in the vapour phase into the liquid alloy causes oversaturation of the liquid alloy, resulting in nucleation and directional nanowire growth [Ref. 6].

nanoparticle) is used to break down and/or concentrate precursors to nucleate nanowire growth.

1.2.1 VLS Growth Mechanism

The Vapor-Liquid-Solid (VLS) growth mechanism describes the role of the catalyst in achieving nanowire growth and is the most common method of obtaining semiconductor nanowires and is illustrated in Figure 1.2. The VLS model was first proposed by Wagner and Ellis in 1964.²⁰ In their original experiment Au particles were placed on a Si {111} substrate and heated to 950°C resulting in droplets of Au-Si alloy. H₂ and SiCl₄ were then introduced into the system. The molten Si-Au acts as a catalyst attracting Si atoms which are then incorporated into the Si-Au alloy. As the drop becomes supersaturated Si begins to precipitate out at the liquid-solid interface between the alloy and substrate. This process continues resulting in a Si nanowire which grows between the substrate and

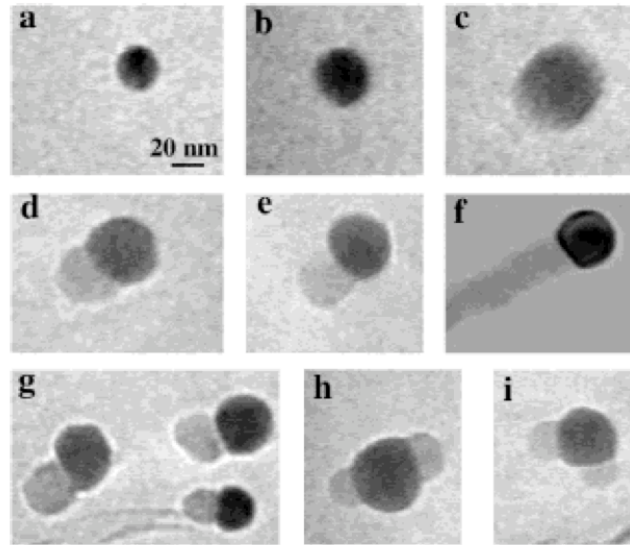


Figure 1.3

In situ TEM images recorded during the process of nanowire growth. (a) Au nanoclusters in solid state at 500 °C; (b) alloying initiates at 800 °C, at this stage Au exists in mostly solid state; (c) liquid Au/Ge alloy; (d) the nucleation of Ge nanocrystal on the alloy surface; (e) Ge nanocrystal elongates with further Ge condensation and eventually a wire forms (f). (g) Several other examples of Ge nanowire nucleation, (h,i) TEM images showing two nucleation events on single alloy droplet [Ref. 25].

catalyst, pushing the catalyst up off the substrate as long as growth conditions, such as temperature, pressure and precursor rates are maintained. Parameters governing the VLS mechanism have been studied extensively.²¹⁻²⁴ In 2001 Yang et al. conclusively verified the validity of the VLS mechanism²⁵ by using a high temperature TEM to directly observe the nucleation of Au catalyzed Ge nanowires. As shown in Figure 1.3, they were able to clearly identify the initial alloying of Au and Ge, followed by nanowire nucleation, and finally axial growth.

While the examples discussed above are for elemental semiconductor nanowires, the VLS mechanism has been used to grow a variety of compound semiconductors nanowires including III/V and II/VI as well as metal-oxide nanowires.

For compound semiconductor materials the additional variable of precursor ratio must also be considered to optimize growth conditions. This variable is particularly important for a variation of VLS known as *self-catalyzed* growth where a liquid globule of one of the nanowire materials, rather than a metallic particle, functions as the nucleation point for nanowire growth. This approach offers the advantage of avoiding the use of a separate metal catalyst and the inherent impurities associated with it. Novotny et al. successfully demonstrated the use self-catalyzed growth to create high purity InP nanowires.⁹ In their experiment a pristine InP substrate is heated prior to growth. The low melting point of indium, combined with the indium rich environment, due to restructuring of the substrate surface and efficient pyrolysis of the indium precursor, result in the formation of liquid indium globules on the substrate. By carefully controlling the III/V ratio it is possible to saturate these In globules and nucleate InP nanowires. The In globule plays an active role in the formation of the wire (as opposed to metal particles which simply facilitate growth) and the III/V ratio is essential for forming and maintaining the globule through the growth process, which in turn will have a strong effect on the diameter and morphology of the resulting nanowire.

1.2.2 Nanowire Heterostructures

The ability to specifically tailor nanowire properties while synthesizing them is one of the more unique characteristics of the bottom up ontology and offers device design options not readily available in planar device structures. Nanowire growth

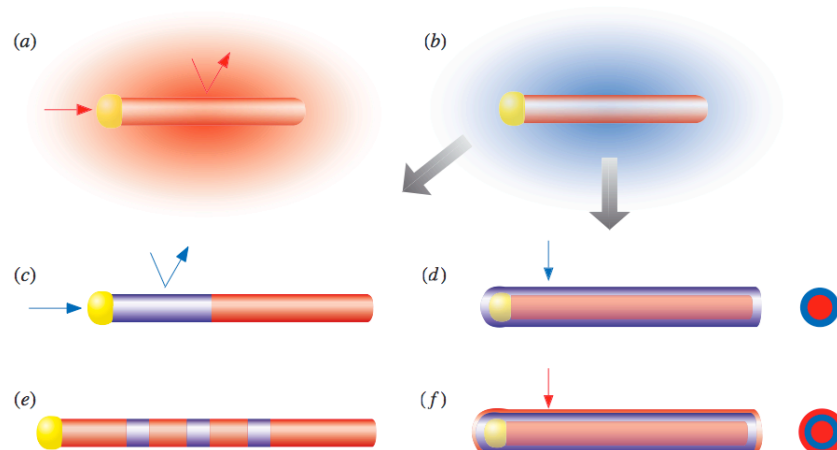


Figure 1.4

Nanowire heterostructure synthesis. (a) Preferential reactant incorporation at the catalyst (growth end) leads to one-dimensional axial growth. (b) A change in the reactant leads to either (c) axial heterostructure growth or (d) radial heterostructure growth depending on whether the reactant is preferentially incorporated (c) at the catalyst or (d) uniformly on the wire surface. Alternating reactants will produce (e) axial superlattices or (f) core-multi-shell structures [Ref. 26].

allows for the incorporation heterostructures along both the length and cross-section of the nanowire. As a result, unique carrier confinement properties can be engineered into a nanowire to adjust and enhance its functionality.²⁶ In this section we will briefly examine the fabrication of such nanowire heterostructures, illustrated in Figure 1.4. Some of their properties and applications will be discussed later in this chapter.

As discussed earlier in this section, axial nanowire growth is achieved by controlling growth conditions such that precursors selectively seek out the nanowire catalyst. Once a nanowire has already been grown it is possible to change growth conditions so there is no longer a preference toward the catalyst and epitaxial material is grown uniformly on the surface of the wire. By altering growth conditions, such as temperature and pressure, as well as changing the available precursors, it is possible to

grow a nanowire of a given material and then coat that nanowire with a shell of a second material. By continuing this process multiple times it is possible to grow multiple layers on a single nanowire resulting in a complex radial structure. These types of structures have been demonstrated^{27,33-34} and are typically referred to as a radial or coaxial heterojunctions.

In addition to the coaxial heterojunctions described above, it is also possible to achieve axial nanowire heterostructures where heterojunctions are formed along the length of the wire.³⁵⁻³⁹ This is achieved by changing precursors while the wire is being grown. This must be done in a careful manner to maintain growth conditions such that the new precursor material will continue to preferentially adsorb at the metal catalyst and thus allow the nanowire to continue to grow. Because the axial growth of nanowires depends on the saturation of the catalyst with precursor material, changing the precursor source abruptly may not result in an abrupt junction.³⁹ Rather it takes some time for the new precursor to saturate the catalyst resulting in a graded axial heterojunction. The graded heterojunction length is expected to be on the order of the diameter of the nanowire catalyst.

1.3 Nanowire Devices and Applications

One-dimensional semiconductor structures are being studied extensively for their applications in electronics,⁶ optoelectronics,⁴⁰ sensing⁴¹ and biology.⁴² Quantum

confinement effects as well as their large surface to volume ratio greatly affect the properties of semiconductor nanowires when compared to their bulk material counterparts. In this section we will briefly examine some of these unique properties and their device applications.

Because carriers in a semiconductor nanowire are quantum confined in two dimensions the band-gap of a nanowire will be different than that of its bulk material counterpart. Thus tailoring the bandgap of a nanowire device for a specific application can be done, not only by selecting the alloy composition⁴³ of the nanowire, but also by careful selection of the nanowire diameter.⁴⁴⁻⁴⁶ In addition, nanowire device dimensions also leads to the possibility of ballistic transport⁴⁷ through one dimensional sub-bands along the length of the wire^{28,48} and could be used to develop highly efficient electronic devices.

While quantum confinement along the width of the wire is inherent to the geometry of a nanowire, quantum confinement can be incorporated along the length of a nanowire by using axial heterojunctions³⁵⁻³⁹ to create novel devices. In 2002 Björk et al. fabricated a resonant tunneling diode using InAs nanowire by including two 5 nm InP barrier layers along the length of the wire.³⁶ In doing so they were able to measure a negative differential resistance with a peak-to-valley ratio of 50:1 at temperatures of 4.2 K.

Nanowire field effect transistors have been constructed in a number of material systems^{30,49-52} in order to better understand and characterize their electrical properties as well as explore their feasibility as a replacement for current planar device

technologies. While there is much room for improvement in this area, interesting device properties have already been observed. In 2007, Dayeh et al. demonstrated the dramatic impact of charged surface states on electron mobility in top-gated InAs nanowire field effect transistors.⁵⁰ Björk et al. observed very large on/off current ratios in vertical InAs nanowire field effect transistors using a surround gate,⁴⁹ which could be optimized for low power logic operations.

The ability to tailor the band gap of a nanowire along with the flexibility of incorporating a core-shell heterostructure to enhance optical and electrical confinement have led to a number of interesting optoelectronic nanowire devices. In 2005 Qian et al. demonstrated the ability to fabricate core-multishell nanowire light emitting diodes (LED) comprised of an n-type GaN core and p-type shell layers incorporating various mole fractions of In and Al.⁵³ The emission spectrum of the LED could be tuned from 365 nm to 600 nm depending on the choice of In incorporation. In 2008 Qian et al. went on to fabricate similar core-multishell nitride based nanowires and successfully demonstrated lasing⁵⁴ with an emission spectra tunable from 365 to 494 nm.

The nanowire geometry allows for efficient collection of photo-generated carriers which is useful in photo-sensing applications, such as photodetectors or photovoltaics. In 2007 Soci et al. demonstrated a UV photodetector with very large gain using ZnO nanowires.⁵⁵ This high gain is attributed surface states which extend the photo-generated carrier lifetimes. Also in 2007, Novotny et al. demonstrated an InP nanowire-polymer hybrid photodiode.⁵⁶ The incorporation of InP nanowires

increased carrier collection efficiencies resulting in high rectification ratios, low ideality factors, and improved reverse saturation current when compared to typical polymer hybrid devices. With proper optimization such devices could provide a promising alternative to current solar cell technologies.

Nanowires have also found various applications in chemistry and biology. Because of their large surface to volume ratio slight perturbations on the surface of the nanowire will greatly alter electrical transport through the nanowire. Because of this nanowires are an ideal candidate for chemical and biological sensors.^{41,42,57-59} By functionalizing the surface of the nanowire to react with a specific molecule the nanowire can be sensitized to selectively detect the presence of that molecule. Furthermore, their size makes nanowires ideal candidates for interfacing with and probing various biological mechanisms at the cellular level. For example, in 2006 Patolsky et al. demonstrated the ability to use Si nanowires to detect, stimulate and inhibit signal propagation in living mammalian neurons.⁶⁰ In 2007 Kim et al. successfully utilized a Si nanowire array to culture stem cells and perform gene delivery.⁶¹ These are just a few examples that suggest the breadth of potential applications for semiconductor nanowires.

1.4 Nanowire Integration

Much progress has been made in the synthesis and characterization of a variety of novel nanowire devices as outlined in the previous sections of this chapter. While

such devices display unique, exploitable properties that may not easily be realized in other, more conventional device geometries, the individual devices have little utility on their own. In order to fully utilize these devices it is necessary to organize and arrange nanowires in some deterministic way in which they can interact with one and other as a system, as well as interface with the outside world.

Nanotechnology affords the flexibility of the bottom-up ontology, which provides unique opportunities in device design but also creates a new set of challenges. In this bottom-up framework we assume the ability to design and build novel nanowire device structures through various synthesis techniques, and then use them as building blocks to develop larger systems. To realize this approach it is necessary to devise clever ways of harvesting and manipulating large numbers of these nanowire building blocks in a highly controlled way. While a number of schemes have been proposed each comes with its own set of trade-offs. In contrast to this approach, a number of top-down approaches to fabricating nanowire systems have also been pursued, which while solving some of the integration issues of the bottom-up approach, impose limits on the methods by which nanowires can be constructed, and as a result, the types of nanowire structures that can be incorporated. In this section we will explore a few nanowire integration schemes including both bottom-up and top-down approaches.

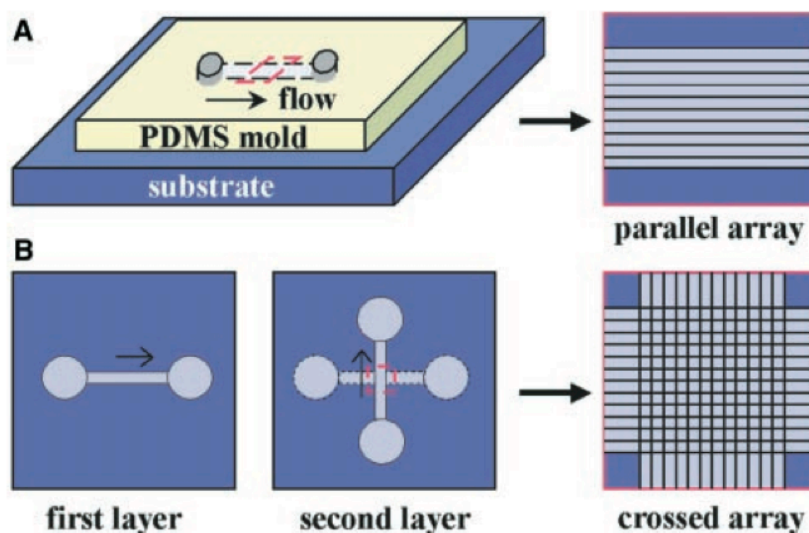


Figure 1.5

Schematic of fluidic assembly. (A) A channel formed when the PDMS mold was brought in contact with a flat substrate. Nanowire assembly was carried out by flowing an nanowire suspension inside the channel with a controlled flow rate for set duration. Parallel arrays of nanowires are observed in the flow direction on the substrate when the PDMS mold is removed. (B) Multiple crossed nanowire arrays can be obtained by changing the flow direction sequentially in a layer-by-layer assembly process [Ref. 63].

1.4.1 Fluidic Assembly

Lieber and Yang both explored the use of microfluidic channels to deliver and align nanowires in a controlled fashion.⁶²⁻⁶⁴ This approach is able to take advantage of the bottom-up ontology in that it is not limited to specific types of wires, or method by which they are fabricated. After they are fabricated, nanowires are suspended in solvent. The solvent is then passed through a polydimethylsiloxane (PDMS) channel over the surface of the substrate, as shown in Figure 1.5. As the solvent flows along the channel wires are aligned in the direction of fluid flow, and then deposited on the substrate while maintaining their orientation. By performing multiple depositions

after re-orienting the direction of the fluid channel Lieber et al. was able to demonstrate the ability to build more complicated structures such as cross-bar arrays.^{63,64} Because this approach is primarily dependent on the anisotropic geometry of a nanowire it can be applied to a wide variety of nanowires. Furthermore this approach allows for the added flexibility of utilizing different nanowire solutions with each subsequent step resulting in perpendicular wires of different types. While this approach does allow for the controlled deposition of parallel and perpendicular nanowires arrays, fluidic assembly is still largely stochastic in that it is impossible to predict exactly where a particular cross-bar array will occur. After the fluidic deposition is complete it is necessary to examine the substrate in the area where channels were previously placed in order to first, find an array of interest, and then perform appropriate processing steps to interface with that array.

1.4.2 Langmuir-Blodgett Technique

Another bottom-up approach uses the Langmuir-Blodgett technique to align large groups of nanowires parallel to one and other⁶⁵⁻⁶⁸ and is illustrated in Figure 1.6. In this approach nanowires are floated on a liquid surface. The walls of the liquid container are then compressed forcing the nanowires into a parallel arrangement, which is then transferred to a substrate. Multiple Langmuir-Blodgett steps can be performed with different substrate orientations resulting in cross-bar arrays. This approach has a number of advantages in that it can cover fairly large areas with parallel nanowires. This approach shares a number of similarities to fluidic assembly.

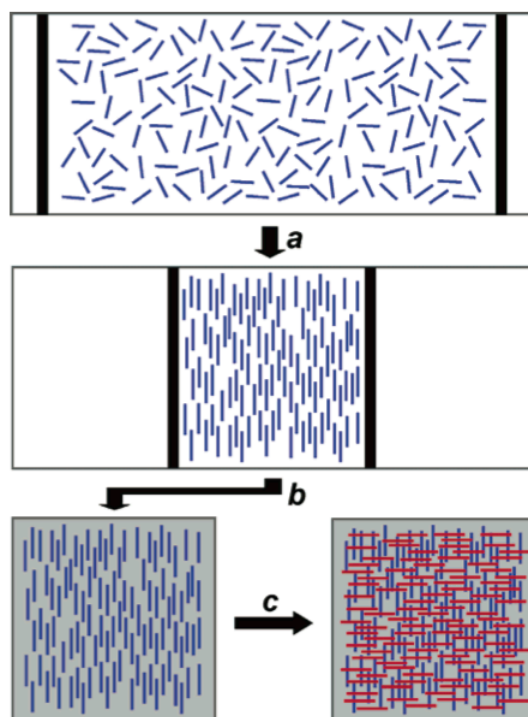


Figure 1.6

Schematic of Langmuir-Blodgett technique. Nanowires (blue lines) in a monolayer of surfactant at the air-water interface are (a) compressed on a Langmuir-Blodgett trough to a specified pitch. (b) The aligned nanowires are transferred to the surface of a substrate to make a uniform parallel array. (c) Crossed nanowire structures are formed by uniform transfer of a second layer of aligned parallel nanowires (red lines) perpendicular to the first layer (blue lines) [Ref. 67].

Like fluidic assembly, this approach is independent of the way in which nanowires are fabricated and only depends on the geometric shape of the nanowire. It also has the flexibility of using different types of wires in subsequent steps allowing for cross-bar arrays where perpendicular wires can be of different types. While Langmuir-Blodgett films do allow the formation of parallel and perpendicular nanowire arrays, there is no way to know exactly where these arrays will form or where the ends of individual wires end up, thus making it difficult to interface with individual wires.

1.4.3 Template Based Assembly

Both bottom-up approaches discussed thus far can be used to assemble arrays of prefabricated nanowires, but at the cost of being able to easily interface those arrays with larger systems. In contrast, a number of top-down approaches have been demonstrated as a way to actually fabricate nanowire devices in an array formation. Typically a macroscopic template is created in order to define where and how a nanowire will be created. Placement of the template deterministically defines exactly where the nanowire array will result and how it can be interfaced with larger systems. In this approach there is a significant trade-off, however, in that only device structures that can be fabricated from a template can be used, thus limiting the approach to certain types of materials or device heterostructures. To better illustrate these trade-offs a few representative examples are discussed.

Jung et al. demonstrated the use of nanoimprint lithography to fabricate a metallic nanowire array.⁶⁹ In their approach a nanoimprint template was used to perform a standard metal evaporation and lift-off. In this way they were able to pattern very fine metallic nanowires with respect to one another and easily integrate them with a larger system for readout. This particular approach, however, is limited to materials that can be evaporated or sputtered. Nanowires with axial or coaxial heterostructures, or complicated doping profiles cannot easily be realized in this approach.

Zhang et al. recently demonstrated Si nanowire photodetector arrays.⁷⁰ They achieved their arrays by first using electron-beam lithography to pattern metal circles

or bars on the surface of an epitaxial wafer. An anisotropic dry etch process was then used to remove material from the wafer resulting in vertical or horizontal nanowires for the circle and bar patterns, respectively. Once again this approach allows a good deal of control over the location and arrangement of the fabricated wires. There is an additional degree of flexibility afforded by the epitaxial wafer. By selecting a wafer with a specific doping profile, or heterostructure, it is possible to use this approach to achieve axial doping profiles or heterostructures along the length of vertical wires. Clever processing or the use of dry transfer techniques⁷¹⁻⁷³ will be necessary in order to create electrically isolated nanowires using this method of wire fabrication. While this approach does afford more flexibility than fabricating nanowires through thin film deposition, it still lacks the ability to easily fabricate coaxial heterostructures or to integrate nanowires of different materials systems.

A number of groups have explored the possibility of using a patterned metal catalyst^{74,75} or oxide^{76,77} as a template for growing vertical nanowire arrays using MOCVD. This approach allows for the creation of vertical nanowire arrays with all the benefits of fabricating nanowires through MOCVD including carefully tailored doping profiles, axial and coaxial heterojunctions. While highly ordered, nanowires that are fabricated in this way will share a common electrical contact at the substrate that may not be desirable. One solution to this may be to use dry transfer techniques⁷¹⁻⁷³ to transfer the array to a new substrate. Another interesting possibility has been explored by Dayeh et al. and is shown in Figure 1.7. In their approach wafer bonding

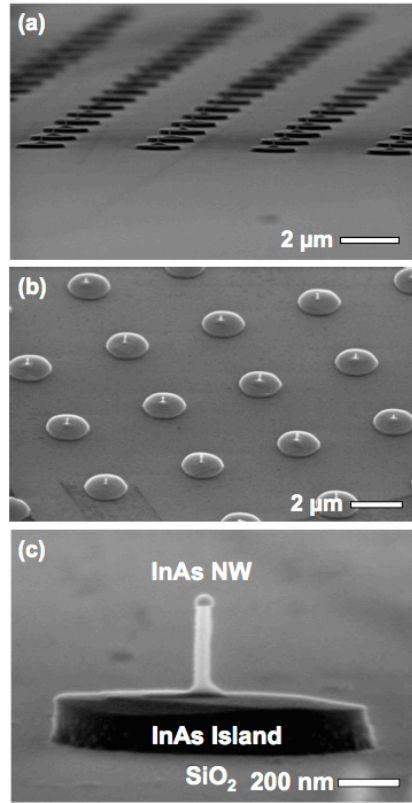


Figure 1.7

An example of patterned catalyst MOCVD grown nanowires on electrically isolated islands achieved through wafer bonding. (a) 85° and (b) 45° angle-view FE-SEM images of vertical and electrically isolated InAs nanowires on SiO₂/Si. (c) Zoom-in FE-SEM image of an InAs NW with an InAs island at its base, sitting on SiO₂ substrate and electrically isolated for individual nanowire addressing [Ref. 78].

is utilized to achieve a substrate that allows for the fabrication of electrically isolated islands, each of which contains one vertical nanowire.⁷⁸

1.4.4 Dielectrophoretic Assembly

Dielectrophoretic assembly refers to the use of carefully tailored electric fields to place nanowires, which are suspended in solution, on predefined electrodes. This approach has been demonstrated to work with a wide variety of nanowires and is the

focus of Chapter 3 of this dissertation. Dielectrophoresis affords the flexibility found in the bottom-up approach where devices can be fabricated by any means. Because the electrodes are fabricated in a top-down approach the final location of the nanowire is deterministic. This compromise between the bottom-up and top-down approach holds great promise for constructing functional nanowire based systems. A more complete introduction to dielectrophoresis and its application in nanowire alignment is presented in Chapter 3 of this dissertation.

References

- ¹ R. Feynman, *Eng. Sci.*, **23**, 22 (1960).
- ² G.E. Moore, *Electronics*, **38**, (1965).
- ³ http://www.itrs.net/Links/2007ITRS/2007_Chapters/2007_ERD.pdf
- ⁴ http://www.itrs.net/Links/2007ITRS/2007_Chapters/2007_ERM.pdf
- ⁵ R. Chau, S. Datta, M. Doczy, B. Doyle, B. Jin, J. Kavalieros, A. Majumdar, M. Metz and M. Radosavljevic, *IEEE Trans. NanoTech.* **4**, 153 (2005).
- ⁶ W. Lu and C. M. Lieber, *J. Phys. D: Appl. Phys.*, **39**, R387 (2006).
- ⁷ M. Yazawa, M. Koguchi, and A. Muto and K. Jiruma, *Adv. Mater.*, **5**, 577 (1993).
- ⁸ K. A. Dick, K. Deppert, L. S. Karlsson, L. R. Wallenberg, L. Samuelson, and W. Seifert, *Adv. Func. Mat.*, **15**, 1603 (2005).
- ⁹ C. J. Novotny, and P. K. L. Yu, *App. Phys. Lett.*, **87**, 203111 (2005).
- ¹⁰ S. Dayeh, E. T. Yu and D. Wang, *NanoLett.*, **7**, 2486, (2007).
- ¹¹ J. L. Liu, S. J. Cai, G. L. Jin, S. G. Thomas and K. L. Wang, *J. Cryst. Growth*, **200**, 106, (1999).
- ¹² V. G. Dubrovskii, G. E. Cirlin, P. I. Soshnikov, A. A. Tonkikh, N. V. Sibirev, Y. B. Samsonenko, and V. M. Ustinov, *Phys. Rev. B*, **71**, 205325 (2005).
- ¹³ L. E. Jensen, M. T. Björk, S. Jeppesen, A. I. Persson, B. J. Ohlsson, and L. Samuelson, *Nano Lett.*, **4**, 1961 (2004).
- ¹⁴ H. D. Park, S. M. Prokes, and R. C. Cammarata, *Appl. Phys. Lett.*, **87**, 063110 (2005).
- ¹⁵ B. Xiang, P. Wei, X. Zhang, S.A. Dayeh, D. P. R. Aplin, C. Soci, D. Yu and D. Wang, *Nano Lett.* **7**, 323 (2007).
- ¹⁶ C. Y. Zhi, X. D. Bai, and E. G. Wang, *Appl. Phys. Lett.*, **85**, 1802 (2004).
- ¹⁷ J. Hu, T. W. Odom, and C. M. Lieber, *Acc. Chem. Res.*, **32**, 435 (1999).

-
- ¹⁸ X. Duan, J. Wang, and C. M. Lieber, *App. Phys. Lett.*, **76**, 1116 (2000).
- ¹⁹ W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.*, **78**, 3304 (2001).
- ²⁰ R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.*, **4**, 89 (1964).
- ²¹ G. A. Bootsma and H. S. Gassen, *J. Cryst. Growth*, **10**, 223, (1971).
- ²² B. Kalache, P. Roca I Cabarrocas, and A. F. Fontcuberta i Morral, *Jpn. J. Appl. Phys.*, **45**, L190 (2006).
- ²³ Z. Chen and C. Cao, *Appl. Phys. Lett.*, **88**, 143118 (2006).
- ²⁴ F. N. Borovik and S. P. Fisenko, *Technical Phys. Lett.*, **33**, 151 (2007).
- ²⁵ Y. Wu and P. Yang, *J. Am. Chem. Soc.*, **123**, 3165 (2001).
- ²⁶ L. J. Lauhon, M. S. Gudiksen and C. M. Lieber, *Phil. Trans. R. Soc. Lond. A*, **362**, 1247 (2004).
- ²⁷ L. J. Lauhon, M. S. Gudiksen, D. Wang, and C. M. Lieber, *Nature*, **420**, 57 (2002).
- ²⁸ W. Lu, J. Xiang, B. P. Timko, Y. Wu, and C. M. Lieber, *Proc. Natl. Acad. Sci. USA*, **102**, 10046 (2005).
- ²⁹ Z. Zanolli, L. E. Fröberg, M. T. Björk, M.-E. Pistol, and L. Samuelson, *Thin Film Solids*, **515**, 793 (2006).
- ³⁰ J. Xiang, W. Lu, Y. Hu, Y. Wu, H. Yan, and C. M. Lieber, *Nature*, **441**, 489 (2006).
- ³¹ X. Jiang, A. Vidan, M. Tinkhan, R. M. Westervelt, and C. M. Lieber, *Nature Nanotechnology*, **1**, 208 (2006).
- ³² X. Jiang, Q. Xiong, S. Nam, F. Qian, Y. Li, and C. M. Lieber, *Nano Lett.*, **7**, 3214 (2007)
- ³³ H.-Y. Li, O. Wunnicke, M. T. Borgström, W. G. G. Immink, M. H. M. Van Weert, M. A. Verheijen, and E. P. A. M. Bakkers, *Nano Lett.*, **7**, 1144 (2007).
- ³⁴ Y. Hu, H. O. H. Churchill, D. J. Reilly, J. Xiang, C. M. Lieber, and C. M. Marcus, *Nature Nanotechnology*, **2**, 622 (2007).

-
- ³⁵ Y. Wu, R. Fan, and P. Yang, *Nano Lett.*, **2**, 83 (2002).
- ³⁶ M. T. Björk, B. J. Ohlsson, C. Thelander, A. I. Persson, K. Deppert, L. R. Wallenberg, and L. Samuelson, *Appl. Phys. Lett.*, **81**, 4458 (2002).
- ³⁷ K. A. Dick, S. Kodambaka, M. C. Reuter, K. Deppert, L. Samuelson, W. Seifert, L. R. Wallenberg, and F. M. Ross, *Nano Lett.*, **7**, 1817 (2007).
- ³⁸ M. Paladugu, J. Zou, Y.-N. Guo, G. J. Auchterlonie, H. J. Joyce, Q. Gao, H. H. Tan, C. Jagadish, Y. Kim, *Small*, **3**, 1873 (2007).
- ³⁹ M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith and C. M. Lieber, *Nature*, **415**, 617 (2002).
- ⁴⁰ P. J. Pauzauskie and P. Yang, *Materials Today*, **10**, 36, (2006).
- ⁴¹ Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science*, **293**, 1289 (2001).
- ⁴² F. Patolsky, B. P. Timko, G. Zheng, and C. M. Lieber, *MRS Bulletin*, **32**, 142 (2007).
- ⁴³ J. Trägårdh, A. I. Persson, J. B. Wagner, D. Hessman and L. Samuelson, *J. Appl. Phys.*, **101**, 123701 (2007).
- ⁴⁴ J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, *Science*, **287**, 1471 (2000).
- ⁴⁵ M. S. Gudiksen, J. Wang, and C. M. Lieber, *J. Phys. Chem. B*, **106**, 4036 (2002).
- ⁴⁶ H. Yu, J. Li, R. A. Loomis, L. W. Wang, and W. E. Buhro, *Nat. Mater.*, **2**, 517 (2003).
- ⁴⁷ R. Landauer, *IBM J. Res. Develop.*, **1**, 223 (1957).
- ⁴⁸ X. Zhou, S. A. Dayeh, D. Aplin, D. Wang, and E. T. Yu, *Appl. Phys. Lett.*, **89**, 053113 (2006).
- ⁴⁹ M. T. Björk, O. Hayden, H. Schmid, H. Riel and W. Riess, *Appl. Phys. Lett.*, **90**, 142110 (2007).
- ⁵⁰ S. A. Dayeh, C. Soci, P. K. L. Yu, E. T. Yu, and D. Wang, *Appl. Phys. Lett.*, **90**, 162112 (2007).
- ⁵¹ Y. Hu, J. Xiang, G. Liang, H. Yan, C. M. Lieber, *Nano Lett.*, **8**, 925 (2008).

-
- ⁵² C. Thelander, L. E. Fröberg, C. Rehnstedt, L. Samuelson, and L.-E. Wernersson, *Elect. Dev. Lett.*, **29**, 206 (2008).
- ⁵³ F. Qian, S. Gradecak, Y. Li, C.-Y. Wen, and C. M. Lieber, *Nano Lett.*, **5**, 2287 (2005).
- ⁵⁴ F. Qian, Y. Li, S. Gradecak, H.-G. Park, Y. Dong, Y. Ding, Z. L. Wang and C. M. Lieber, *Nature Materials*, **7**, 701 (2008).
- ⁵⁵ C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, J. Park, X.Y. Bao, Y.H. Lo, D. Wang, *Nano Lett.*, **7**, 1003 (2007).
- ⁵⁶ C. J. Novotny, E. T. Yu, and P. K. L. Yu, *Nano Lett.*, **8**, 775 (2008).
- ⁵⁷ M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, *Angew. Chem. Int. Ed.*, **41**, 2405 (2002).
- ⁵⁸ Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, *Nano Lett.*, **4**, 245 (2004).
- ⁵⁹ M. C. McApline, H. Ahmad, D. Wang and J. R. Heath, *Nature Materials*, **6**, 379 (2007).
- ⁶⁰ F. Patolsky, B. P. Timko, G. Yu, Y. Fang, A. B. Greytak, G. Zheng, and C. M. Lieber, *Science*, **313**, 1100 (2006).
- ⁶¹ W. Kim, J. K. Ng, M. E. Kunitake, B. R. Conklin, and P. Yang, *J. A. Chem. Soc.*, **129**, 7228 (2007).
- ⁶² B. Messer, J. H. Song, and P. Yang, *J. Am. Chem. Soc.*, **122**, 10232 (2000).
- ⁶³ Y. Huang, X. Duan, Q. Wei, and C. M. Lieber, *Science*, **291**, 630 (2001).
- ⁶⁴ Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber **294**, 1313 (2001).
- ⁶⁵ F. Kim, S. Kwan, J. Akana, and P. Yang, *J. Am. Chem. Soc.* **123**, 4360 (2001).
- ⁶⁶ A. Tao, F. Kim, C. Hess, J. Goldberger, R. He, Y. Sun, Y. Xia, and P. Yang, *Nano Lett.*, **3**, 1229 (2003).
- ⁶⁷ D. Whang, S. Jin, Y. Wu, and C. M. Lieber, *Nano Lett.*, **3**, 1255 (2003).

-
- ⁶⁸ P. Yang, *Nature*, **425**, 243 (2003).
- ⁶⁹ G. Y. Jung, S. Ganapathiappan, X. Li, D. A. A. Ohlberg, D. L. Olynick, Y. Chen, W. M. Tong and R. S. Williams, *Appl. Phys. A*, **78**, 1169 (2004).
- ⁷⁰ A. Zhang, S. You, C. Soci, Y. Liu, D. Wang and Y.-H. Lo, *Appl. Phys. Lett.*, **93**, 121110 (2008).
- ⁷¹ Y. Sun and J. A. Rogers, *Nano Lett.*, **4**, 1953 (2004).
- ⁷² A. Javey, S. Nam, R. S. Friedman, H. Yan and C. M. Lieber, *Nano Lett.*, **7**, 773 (2007).
- ⁷³ Z. Fan, J. C. Ho, Z. A. Jacobson, R. Yerushalmi, R. L. Alley, H. Razavi and A. Javey, *Nano Lett.*, **8**, 20 (2008).
- ⁷⁴ A. I. Hochbaum, R. Fan, R. He and P. Yang, *Nano Lett.*, **5**, 457 (2005).
- ⁷⁵ H. J. Fan, W. Lee, R. Scholz, A. Dadgar, A. Krost, K. Nielsch and M. Zacharias, *Nanotechnology*, **16**, 913 (2005).
- ⁷⁶ J. Motohisa, J. Noborisaka, J. Takeda, M. Inari and T. Fukui, *J. Cryst. Growth*, **272**, 180 (2004).
- ⁷⁷ L. E. Jensen, M. T. Bjrk, S. Jeppesen, A. I. Persson, B. J. Ohlsson, and L. Samuelson, *Nano Letters*, **4**, 1961 (2004).
- ⁷⁸ S. A. Dayeh, “Semiconductor Nanowires for Future Electronics: Growth, Characterization, Device Fabrication, and Integration”, Doctoral Dissertation, University of California San Diego (2008).

Chapter 2

Critical Dimensions in Coaxial Nanowire Heterostructures

2.1 Introduction

Planar layers of different semiconductor materials are commonly used in semiconductor device technologies to build electronic and optoelectronic devices. In designing and growing multilayered device structures it is important to select material and dimensional parameters, not only to achieve the desired electronic and optoelectronic device properties, but also to avoid degradation in device performance and reliability due to the presence of dislocations.

A given semiconductor material or alloy composition offers a device designer certain properties, such as a specific band gap or refractive index, but with those properties also comes a specified lattice constant. Figure 2.1 shows the lattice constant and energy gap for a number of common semiconductor materials and their alloys. From this plot it is clear that selecting materials of different bandgaps will often result in materials of different lattice constant. In order to maintain a perfect, dislocation free, semiconductor crystal using two materials of differing lattice constant it is necessary for the two crystals to accommodate the lattice mismatch strain between these two materials. The process by which this occurs is described below and illustrated in Figure 2.2.

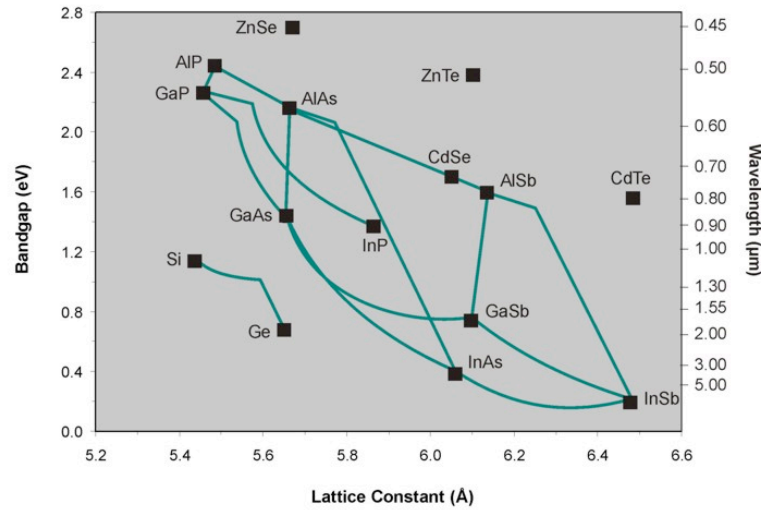


Figure 2.1

Plot of energy bandgaps and lattice constants for various semiconductor materials and their alloys [Ref. 1].

The lattice mismatch between an epitaxial layer and its substrate typically requires the lattice constant of the epitaxial layer to conform to that of the substrate in order to maintain a perfect, dislocation free, heterointerface. To do this the lattice of the epitaxial layer must deform from its relaxed state resulting in stored potential energy in the layer, much like the potential energy stored in spring when it is compressed. Because this energy scales with volume, as the epitaxial layer is grown the amount of strain energy stored in the layer also increases. The system will tend to prefer to exist in the lowest possible energy state. As such we would expect the epitaxial layer to want to relax to its own lattice constant, much like a compressed spring wishes to return to its normal state. This can only occur, however, through the formation of dislocations at the heterointerface. Such dislocations also have a strain field associated with them, thus there is a trade off between the strain energy stored in

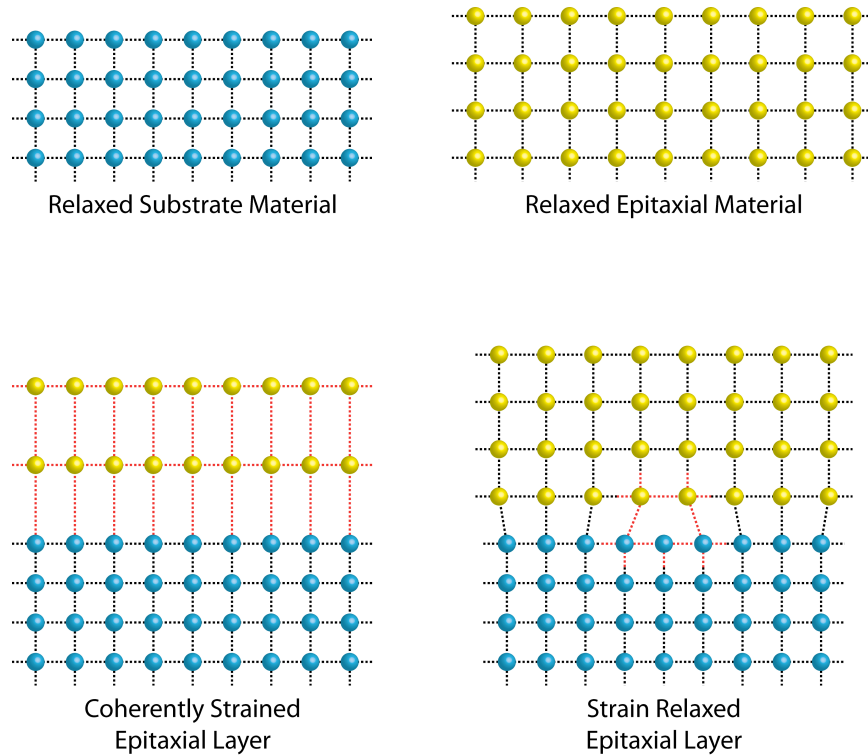


Figure 2.2

Schematic depictions of relaxed substrate material (top left) and relaxed epitaxial material (top right) with different lattice constants. In a coherently strained epitaxial layer (bottom left) the epitaxial film is forced to conform to the lattice constant of the substrate resulting in strain throughout the epitaxial layer. In a strain relaxed epitaxial layer the layer has gotten sufficiently thick that the strain energy stored in the coherently strained film becomes too great and it becomes energetically favorable to include a dislocation at the interface resulting in a local strain field but allowing the rest of the epitaxial layer to relax.

the deformed epitaxial layer versus the strain energy associated with dislocations at the heterointerface. As an epitaxial layer is grown on a substrate there will be a certain epitaxial layer thickness at which the strain energy stored in the layer becomes too great, and it becomes energetically favorable to insert dislocations at the heterointerface allowing the layer as a whole to relax at the expense of introducing local strain fields around the interface dislocations. The film thickness at which this occurs is known as the *critical thickness*, the thickness at which an epitaxial layer

loses coherence with the substrate. The critical thickness can be calculated by either considering forces associated with interfacial dislocations^{2,3} or by considering the energetics associated with strain in the system.⁴ Both approaches yield the same result in defining the relationship between lattice mismatch strain and critical thickness.⁵ This relationship has been studied extensively and serves as an accurate predictor of feasible layer structures in planar epitaxial growth.

As outlined Chapter 1, successes in the growth and fabrication of semiconductor nanowires^{6,7} have led to new opportunities in novel device design for applications in electronics,⁸⁻¹³ optoelectronics,^{14 -18} sensing¹⁹⁻²² and biology.^{23 -25} Many of these devices either require, or can benefit from, the use of heterostructures in their design, and nanowire heterostructures in both coaxial^{9,26-32} and axial^{8,33-36} geometries have been proposed to optimize device performance. In determining the feasibility of these designs it is necessary to consider the strain that arises in heterostructures due to the lattice mismatch between materials. Such strain not only affects the electronic and optical properties of the device, but also determines the device dimensions at which coherence is lost and dislocations form, which will significantly alter or degrade device performance. Furthermore, the types of dislocations or other defects by which relaxation occurs will vary between crystal structures mandating analysis specific to each possible crystal structure.

Only a limited amount of work has been done previously to model coherence and critical dimensions in nanowire structures. A number of models have been proposed to study both coaxial,³⁷⁻³⁹ and axial^{40,41} critical dimensions, but the vast

majority do so without considering specific crystallographic orientations of semiconductor nanowires, which will impact the specific mechanism by which relaxation occurs. In this chapter we provide a methodology for determining coherent geometries in coaxial nanowire heterostructures based on the formalism commonly used in thin film heteroepitaxy.²⁻⁵ This model is designed to provide a framework from which to determine the structural feasibility of various coherently strained core-shell nanowire structures. Illustrative calculations are presented for specific crystal structures and materials. The results of these explorations are expected to serve as a guide for semiconductor device engineers to determine the feasibility of various core-shell structures that may be of interest. With some care this basic method can be extended to other semiconductor material systems.

2.2 Analytical Framework

The geometry of the nanowire system considered is shown in Figure 2.3. The nanowire consists of a core material of radius r and shell material of thickness h . The axis of the wire is assumed to be along the $[111]$ direction for zinc blende structures and along the $[0001]$ direction for wurtzite structures. In both cases the coherence requirement between the core and shell will result in cross-sectional and longitudinal strain components due to the mismatch in lattice parameters along the length of the wire as well as around the cylindrical surface of the wire.

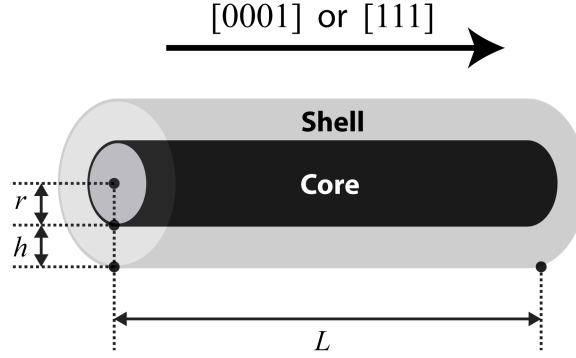


Figure 2.3

Schematic diagram of core-shell nanowire heterostructure where r , h , and L represent the core radius value, the shell thickness value, and the length of the wire respectively. The nanowire is assumed to be oriented along the $[0001]$ direction for wurtzite nanowires and the $[111]$ direction for zinc blende nanowires.

In this analysis we are interested in determining the geometric limits at which coherence is lost in an analytical fashion that provides guidance and can be easily translated between material systems. A commonly used methodology to predict coherency limits in planar structures examines the strain energy of the system and determines the film thickness at which it becomes energetically favorable to relieve lattice strain by inserting a dislocation.²⁻⁵ We will employ a similar approach to determine the coherency limits of the coaxial nanowire heterostructure.⁴² We first solve for the lattice mismatch strain energy in the system, then determine the energetics associated with dislocations that are likely to form, and finally, determine the geometric limits at which it becomes favorable for these dislocations to appear. In contrast to the planar case, the geometry of the coaxial nanowire along with the comparable volumes of the core and shell regions require that the dimensions of both the core and the shell be considered. This gives rise to the idea of critical dimensions:

combinations of core and shell dimensions that will lead to stable, coherently strained structures. This analysis considers only strain energies due to lattice mismatch and dislocations, and does not take into account the effects of faceting or other surface energy effects. For sufficiently large structures these effects are not expected to significantly alter the outcome of the calculation. For smaller structures where these effects could contribute more significantly to strain relaxation behavior, the analytical approach presented here must be supplemented by a much more detailed and likely numerical approach.

In general it is found that the nanowire geometry is more forgiving than its thin film counterpart in that a number of dimensional choices exist to attain a stable coherent structure. For a given choice of materials and alloy compositions there exists a critical core radius, below which the structure is always coherent regardless of shell thickness. Structures with a core radius greater than this critical value can still be stable provided that the shell thickness is below a critical shell thickness value. The critical shell thickness is dependent on the core radius and will vary depending on the material system being considered. The critical dimensions are found to be dependent only on core radius and shell thickness and have no dependence on the length of the wire.

Liang et al approached the problem in a similar manner.³⁸ Their model suggests that the nanowire system should be about 20% less tolerant of strain than the calculations presented in here. This is likely due to the differing methodologies used to calculate coherent strain energy in the two models. Both approaches are derived

from similar principles and as a result the difference between the two models become insignificant for nanowires larger than 25 nm or so.

2.2.1. Coherent Strain Energy Calculation

Elastic theory and the well-known relations between stress and strain can be used to develop analytical expressions for strain energy in coaxial nanowire heterostructures. The nanowire structure is taken to be perfectly round with smooth surfaces and interfaces, thus neglecting any effects of faceting. This is done in order to apply a straight-forward analytical approach to the problem and is not expected to significantly alter the calculation for sufficiently large structures. The derivations presented here are specific to wurtzite nanowires oriented along the $[0001]$ direction as well as zinc blende wires oriented along the $[111]$ direction. Analogous derivations can be carried out for other material systems provided the elastic stiffness tensor is isotropic in the cross-sectional plane of the wire. If the cross-section of the wire were anisotropic it is likely that the shape of the wire would change to accommodate strain, thus violating assumptions used in this computation.

In planar thin film growth, the strain energy is calculated by assuming a number of geometric boundary conditions and using them to calculate the full strain field within the structure. The basic boundary conditions in planar thin film growth define two perpendicular in-plane strain components arising from lattice mismatch and a stress component normal to the interface, as shown in Figure 2.4 (a). In the coaxial nanowire geometry an analogous approach can be used, as illustrated in Figure 2.4 (b).

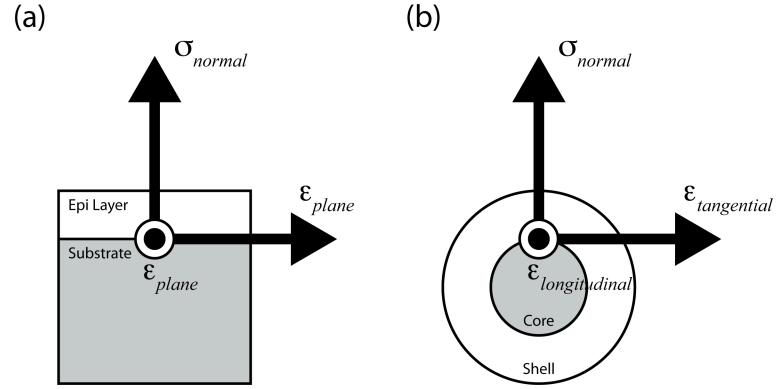


Figure 2.4

Diagram of the orientation of stress (σ) and strain (ϵ) components in (a) planar heterostructures and (b) coaxial heterostructures.

At a single point on the cylindrical heterointerface it is possible to define two perpendicular strain components due to lattice mismatch - one component along the length of the wire ($\epsilon_{longitudinal}$) and the other tangential to the heterointerface ($\epsilon_{tangential}$). The stress normal to the heterointerface, σ_{normal} , at that particular point is analogous to the stress in the growth direction in the planar case. Thus, by defining a cartesian coordinate system comprised of a longitudinal, tangential and normal axis for a specific point on the nanowire heterointerface it is possible to apply the planar formalism to solve for the full strain field at that point. By applying this approach to every point on the heterointerface it is then possible to construct the full strain field within the system and subsequently to calculate the strain energy.

To implement this approach, it is necessary to specify an appropriately oriented cartesian coordinate system for each point on the interface. This is accomplished by rotating the reference axis (denoted by x , y , z) as shown in Figure

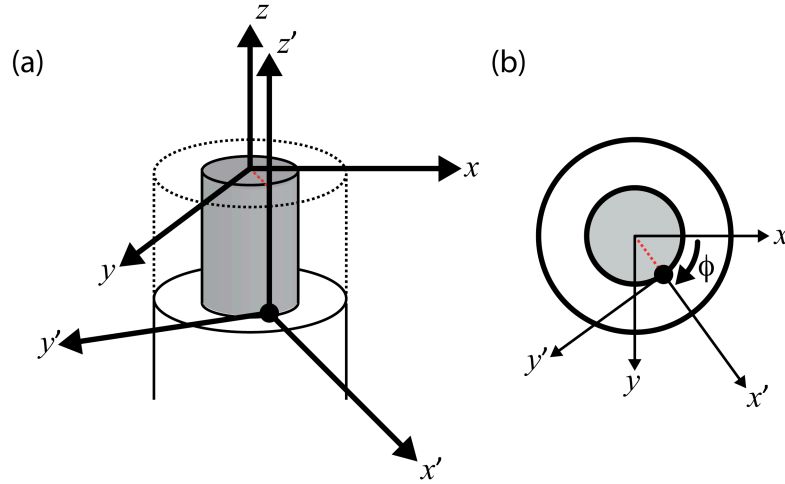


Figure 2.5

(a) Cutaway and (b) cross-sections of coaxial nanowire structure. $\{x, y, z\}$ denote the reference axes of the system while $\{x', y', z'\}$ denote the normal, tangential and longitudinal axes for a specific point on the circular interface corresponding to the angle ϕ .

2.5. If we specify a point on the interface at an angle ϕ relative to the reference axis, x , the specific cartesian axes for that point (denoted by x' , y' , z') can be obtained by rotating the reference axes by an angle ϕ about the z axis. Longitudinal (z'), tangential (y'), and normal (x') boundary conditions, similar to those used in the planar formalism, can now be applied at that point on the interface.

In planar thin film growth the top surface of the structure is unconstrained, allowing the film thickness to expand or contract as needed to accommodate strain. This can be expressed as a boundary condition that states there be no stress in the direction normal to the heterointerface.²⁻⁵ In the coaxial nanowire geometry there is nothing constraining the outer surface of the nanowire system, thus the radius of the system is free to expand or contract in order to accommodate strain. For a particular point on the interface this yields the boundary condition that there be no stress in the

direction normal to the heterointerface at that point. The wire is assumed to be of infinite length and thus the effects of the circular faces at either end of the wire are not considered.

Using standard matrix notation it is possible to write the elements of stress as a function of the strain and the elastic stiffness matrix for a given material.⁴³ These elements of stress and strain can then be re-written in their tensor forms. Rotating these tensors about the z axis by an angle ϕ will yield expressions relating the normal, tangential, and longitudinal components of stress and strain for a given point on the interface, denoted by the angle ϕ . The normal, tangential, and longitudinal boundary conditions defined earlier can then be applied to elements of the rotated tensors as follows:

$$\sigma'_1(c_{ij}, \epsilon_i, \phi) = 0, \quad (2.1)$$

$$\epsilon'_2(\epsilon_i, \phi) = f_t, \quad (2.2)$$

$$\epsilon'_3 = \epsilon_3 = f_l, \quad (2.3)$$

where σ'_1 represents the rotated stress tensor element normal to the interface at a point specified by the angle ϕ , c_{ij} represent various elements of the elastic stiffness matrix of the material being considered, f_t and f_l represent the differential lattice mismatch strain in the tangential and longitudinal direction, respectively, ϵ_i represents strain matrix elements relative to the reference axis, and ϵ'_2 and ϵ'_3 represent the rotated strain tensor elements tangential to the interface at the specified point and along the length of the wire at the specified point, respectively.

For planar growth it is also assumed that the strain components are perfectly perpendicular and that there are no shear strains that arise from lattice mismatch.²⁻⁵ As in the planar case, for a single point on the heterointerface there will be no shear strain components relative to the normal, tangential and longitudinal directions. These conditions can be expressed as follows:

$$\varepsilon'_4(\varepsilon_i, \phi) = 0, \quad (2.4)$$

$$\varepsilon'_5(\varepsilon_i, \phi) = 0, \quad (2.5)$$

$$\varepsilon'_6(\varepsilon_i, \phi) = 0, \quad (2.6)$$

where ε'_4 , ε'_5 and ε'_6 , represent the shear strain elements between the tangential and longitudinal axes, normal and longitudinal axes, and the normal and tangential axes respectively.

From Eqs. (2.1)-(2.6) a complete solution for the strain field ε_i can be obtained as a function of angular position ϕ . The resulting expression for the strain field can then be used to compute the strain energy density $w = \frac{1}{2} c_{ij} \varepsilon_i \varepsilon_j$, which integrated over the volume of the material will yield an expression for the total strain energy.⁴³

2.2.1.1 Strain Energy in Wurtzite Nanowires

In order to calculate the coherent strain energy stored in the core and shell regions of a wurtzite nanowire, it is necessary to explicitly describe the strain field present throughout the coaxial nanowire due to lattice mismatch strain. This can be

done by applying the formalism described above. The stress and strain tensors for a solid are given by

$$\sigma = \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{bmatrix}, \quad (2.7)$$

and

$$\varepsilon = \begin{bmatrix} \varepsilon_1 & \frac{1}{2}\varepsilon_6 & \frac{1}{2}\varepsilon_5 \\ \frac{1}{2}\varepsilon_6 & \varepsilon_2 & \frac{1}{2}\varepsilon_4 \\ \frac{1}{2}\varepsilon_5 & \frac{1}{2}\varepsilon_6 & \varepsilon_3 \end{bmatrix}, \quad (2.8)$$

respectively. The relationship between stress and strain is described by the elastic stiffness tensor, c , for a given material. With simplified notation this relationship can be described by the following expression,

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} \quad (2.9)$$

for a wurtzite crystal. Using eqs. (2.9) it is possible to write each stress element as a function of elements of the strain tensor and elastic stiffness tensor. The stress and strain tensors can now be written as

$$\varepsilon = \begin{bmatrix} \varepsilon_1 & \frac{1}{2}\varepsilon_6 & \frac{1}{2}\varepsilon_5 \\ \frac{1}{2}\varepsilon_6 & \varepsilon_2 & \frac{1}{2}\varepsilon_4 \\ \frac{1}{2}\varepsilon_5 & \frac{1}{2}\varepsilon_6 & \varepsilon_3 \end{bmatrix}, \quad (2.10)$$

and

$$\sigma = \begin{bmatrix} \sigma_1(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{11}, c_{12}, c_{13}) & \sigma_6(\varepsilon_6, c_{11}, c_{12}) & \sigma_5(\varepsilon_5, c_{44}) \\ \sigma_6(\varepsilon_6, c_{11}, c_{12}) & \sigma_2(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{11}, c_{12}, c_{13}) & \sigma_4(\varepsilon_4, c_{44}) \\ \sigma_5(\varepsilon_5, c_{44}) & \sigma_4(\varepsilon_4, c_{44}) & \sigma_3(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{13}, c_{33}) \end{bmatrix}, \quad (2.11)$$

respectively. The tensors thus far have been written with respect to the reference axes shown in shown in Figure 2.5. In order to solve for the strain components at a given point at the heterointerface it is necessary to rotate these tensors by an arbitrary angle, ϕ , which corresponds to a point on the heterointerface. Using the standard rotation matrix,

$$\alpha_{rotation} = \begin{bmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (2.12)$$

it is possible to calculate elements for the rotated stress and strain tensors, σ' and ε' , respectively, given by

$$\varepsilon' = \begin{bmatrix} \varepsilon_1(\phi) & \frac{1}{2}\varepsilon_6(\phi) & \frac{1}{2}\varepsilon_5(\phi) \\ \frac{1}{2}\varepsilon_6(\phi) & \varepsilon_2(\phi) & \frac{1}{2}\varepsilon_4(\phi) \\ \frac{1}{2}\varepsilon_5(\phi) & \frac{1}{2}\varepsilon_4(\phi) & \varepsilon_3 \end{bmatrix} \quad (2.13)$$

and

$$\sigma' = \begin{bmatrix} \sigma_1(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{11}, c_{12}, c_{13}, \phi) & \sigma_6(\varepsilon_6, c_{11}, c_{12}, \phi) & \sigma_5(\varepsilon_5, c_{44}, \phi) \\ \sigma_6(\varepsilon_6, c_{11}, c_{12}, \phi) & \sigma_2(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{11}, c_{12}, c_{13}, \phi) & \sigma_4(\varepsilon_4, c_{44}, \phi) \\ \sigma_5(\varepsilon_5, c_{44}, \phi) & \sigma_4(\varepsilon_4, c_{44}, \phi) & \sigma_3(\varepsilon_1, \varepsilon_2, \varepsilon_3, c_{13}, c_{33}) \end{bmatrix}. \quad (2.14)$$

The elements of the rotated stress and strain tensor can now be written explicitly for an arbitrary point on the heterointerface, specified by the angle ϕ , only as a function of

the non-rotated strain elements and the elastic stiffness tensor elements. For a given point on the heterointerface the value of any unknown elements in the strain tensor can now be explicitly solved for by applying the appropriate boundary conditions, described earlier and given by,

$$\sigma'_1(c_{ij}, \varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_6, \phi) = 0, \quad (2.15)$$

$$\varepsilon'_2(\varepsilon_1, \varepsilon_2, \varepsilon_6, \phi) = f_t, \quad (2.16)$$

$$\varepsilon'_3 = \varepsilon_3 = f_l, \quad (2.17)$$

$$\varepsilon'_4(\varepsilon_4, \varepsilon_5, \phi) = 0, \quad (2.18)$$

$$\varepsilon'_5(\varepsilon_4, \varepsilon_5, \phi) = 0, \quad (2.19)$$

$$\varepsilon'_6(\varepsilon_1, \varepsilon_2, \varepsilon_6, \phi) = 0. \quad (2.20)$$

Once each element of the strain tensor, ε , can be solved for and written as a function of known quantities (c_{ij} , f_t , f_l and ϕ), it can be applied to calculate the total strain energy stored in the core and shell regions using the expressions,

$$U = \int_0^L \int_0^r \int_0^{2\pi} \frac{1}{2} c_{ij} \varepsilon_i \varepsilon_j \rho \, d\phi \, d\rho \, dz \quad (2.21)$$

and

$$U = \int_0^L \int_r^{(r+h)} \int_0^{2\pi} \frac{1}{2} c_{ij} \varepsilon_i \varepsilon_j \rho \, d\phi \, d\rho \, dz, \quad (2.22)$$

respectively. Applying this methodology, the coherent strain energy expressions for the core and shell regions of a wurtzite nanowire are found to be

$$U_w^{(i)} = \frac{\left(c_{11}^{(i)} f_t^{(i)}\right)^2 - \left(c_{12}^{(i)} f_t^{(i)} + c_{13}^{(i)} f_l^{(i)}\right)^2 + c_{11}^{(i)} f_l^{(i)} \left(c_{13}^{(i)} f_t^{(i)} + c_{33}^{(i)} f_l^{(i)}\right)^2}{2c_{11}^{(i)}} L\pi[r^2] \quad (2.23)$$

and

$$U_w^{(ii)} = \frac{\left(c_{11}^{(ii)} f_t^{(ii)}\right)^2 - \left(c_{12}^{(ii)} f_t^{(ii)} + c_{13}^{(ii)} f_l^{(ii)}\right)^2 + c_{11}^{(ii)} f_l^{(ii)} \left(c_{13}^{(ii)} f_t^{(ii)} + c_{33}^{(ii)} f_l^{(ii)}\right)^2}{2c_{11}^{(ii)}} \times \quad (2.24)$$

$$L\pi\left[(r+h)^2 - r^2\right],$$

respectively. In general, variables with superscripts (i) and (ii) will denote parameters specific to the core and shell materials, respectively.

For a nanowire with a wurtzite crystal structure oriented with its $[0001]$ direction along the long axis the longitudinal strain components will be imposed by the c -axis lattice parameter mismatch between the core and shell materials. The longitudinal strain component in the core material is given by

$$f_l^{(i)} = \frac{c - c^{(i)}}{c^{(i)}}, \quad (2.25)$$

where c represents the strained lattice constant of the system and $c^{(i)}$ represents the unstrained lattice parameter of the core material. The longitudinal strain component in the shell material is given by

$$f_l^{(ii)} = \frac{c - c^{(ii)}}{c^{(ii)}}, \quad (2.26)$$

where $c^{(ii)}$ represents the unstrained lattice parameter of the shell material.

For a nanowire with a wurtzite crystal structure oriented with its $[0001]$ direction along the long axis, the strain within the cross-section is governed by a tangential lattice mismatch strain component at each point on the heterointerface. In the core material, this strain component is given by

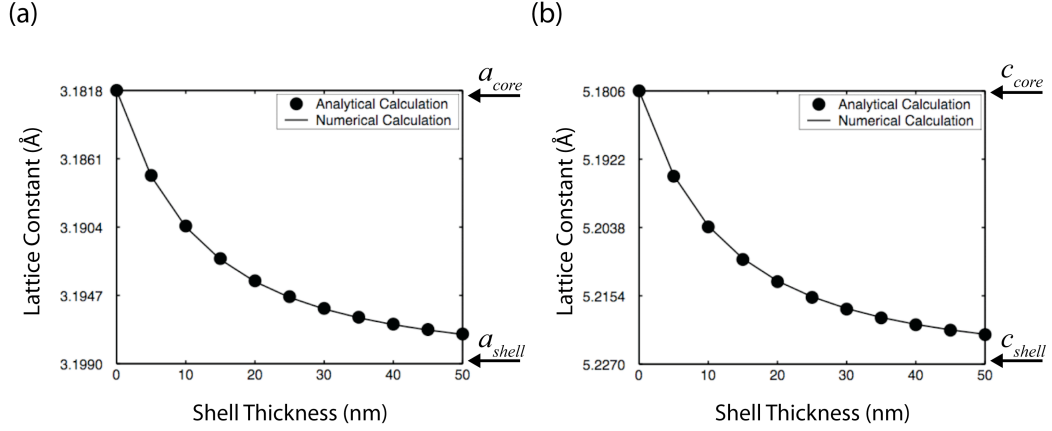


Figure 2.6

Plot of the (a) cross-sectional equilibrium lattice constants a and (b) longitudinal lattice constant c as functions of shell thickness. The structure considered is comprised of a 25 nm GaN core and an $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ shell. The maximum and minimum y axis values on both plots are set to be the relaxed core and shell lattice constants, respectively. The points show calculated values achieved through energy minimization. The line shows the results of the analytical model presented in Eq. (2.31).

$$f_t^{(i)} = \frac{a - a^{(i)}}{a^{(i)}}, \quad (2.27)$$

where a represents the strained lattice constant of the system and $a^{(i)}$ represents the unstrained lattice parameter of the core material. Similarly, the tangential strain component in the shell material at a given point along the circular interface is given by

$$f_t^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}}, \quad (2.28)$$

where $a^{(ii)}$ represents the unstrained lattice parameter of the shell material.

For a given geometry and material composition the strained lattice constants of system, a and c , will assume values that minimize the total strain energy. For this reason we will refer to a and c as the equilibrium lattice constants. In order to determine the values for the equilibrium lattice constants we must minimize $U_{\text{strain}} = U^{(i)} + U^{(ii)}$ with respect to a and c by using the strain expressions given in

Eqs. (2.25)-(2.28). This minimization cannot be performed simultaneously for both a and c using analytical methods. Figure 2.6 shows values for a and c obtained by numerical minimization in a coaxial heterostructure with a 25 nm radius GaN core, as a function of thickness of an $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ shell. The lattice constants and elastic stiffness constants used in the computation were taken from Ref. 44 and are all assumed to vary linearly with alloy composition.

The numerical results in Figure 2.6 show that the equilibrium lattice constants will fall somewhere between the relaxed core and shell values, and will tend toward those of the region with greater volume. This is expected given the proportional relationship between strain energy and crystal volume seen in Eqs. (2.23) and (2.24). These results show that for a given choice of material, geometry will determine the distribution of lattice strain between the core and shell materials. It is because of this that the dimensions of both core and shell must be considered in determining stable coherent geometries.

An analytical expression for the equilibrium lattice constant can provide a more intuitive understanding of how the core and shell dimensions affect the strain distribution between the two regions. From the numerical results shown in Figure 2.6 it appears that the equilibrium lattice constants a and c have the same functional dependence on shell thickness when normalized to their respective relaxed core and shell lattice values, i.e.,

$$f_t^{(i)} = f_l^{(i)} = f^{(i)} = \frac{p - p^{(i)}}{p^{(i)}}, \quad (2.29)$$

$$f_t^{(ii)} = f_l^{(ii)} = f^{(ii)} = \frac{p - p^{(ii)}}{p^{(ii)}}, \quad (2.30)$$

where p represents an equilibrium value for a generic lattice constant variable, $p^{(i)}$ represents the relaxed value of the corresponding generic core lattice constant, and $p^{(ii)}$ represents the relaxed value of a generic shell lattice constant. Substituting Eqs. (2.29) and (2.30) into U_{strain} and minimizing with respect to p yields

$$p = \frac{p^{(ii)} p^{(i)} (p^{(ii)} r^2 \chi^{(i)} + p^{(i)} h (h + 2r) \chi^{(ii)})}{p^{(ii)} r^2 \chi^{(i)} + p^{(i)2} h (h + 2r) \chi^{(ii)}}, \quad (2.31)$$

where $\chi^{(i)}$ and $\chi^{(ii)}$ are given by

$$\chi_{wurtzite} = \frac{c_{11}^2 - (c_{12} + c_{13})^2 + c_{11}(2c_{13} + c_{33})}{2c_{11}}. \quad (2.32)$$

Eq. (2.31) defines the behavior of the equilibrium lattice constant relative to the relaxed core and shell lattice parameters. Figure 2.6 shows that the analytical functions are in good agreement with the numerical results, confirming that Eq. (2.31) is an appropriate approximation for the equilibrium lattice constant.

2.2.1.2 Strain Energy in Zinc Blende Nanowires

In order to use this methodology to calculate the coherent strain energy in [111] zinc blende coaxial nanowire structures it is necessary to define an appropriately oriented elastic stiffness matrix, c_{ij} , and proper longitudinal and tangential lattice mismatch boundary conditions. Because the zinc blende nanowire is assumed to be oriented along the [111] direction, it is necessary to rotate c_{ij} such that the z-axis of c_{ij}

is parallel to the $[111]$ direction. This must be done in order to make sure the normal, tangential and longitudinal boundary constraints are oriented properly with respect to the crystal structure. The coherent strain energy expressions for the core and shell regions of a zinc blende nanowire are then given by

$$U_{ZB}^{(i)} = \frac{A^{(i)}(f_t^{(i)})^2 + B^{(i)}f_t^{(i)}f_l^{(i)} + C^{(i)}(f_l^{(i)})^2}{D^{(i)}} L\pi[r^2] \quad (2.33)$$

and

$$U_{ZB}^{(ii)} = \frac{A^{(ii)}(f_t^{(ii)})^2 + B^{(ii)}f_t^{(ii)}f_l^{(ii)} + C^{(ii)}(f_l^{(ii)})^2}{D^{(ii)}} L\pi[(r+h)^2 - r^2], \quad (2.34)$$

respectively, where f_t and f_l represent the tangential and longitudinal strain constraints, A, B, C and D are given by

$$A = c_{11}^2 - 2c_{12}^2 + 40c_{12}c_{44} + 16c_{44}^2 + c_{11}(c_{12} + 26c_{44}), \quad (2.35)$$

$$B = 4(c_{11} - 2c_{12} - 2c_{44})(c_{11} - c_{12} + 4c_{44}), \quad (2.36)$$

$$C = 4(c_{11} + 2c_{12} + c_{44})(c_{11} - c_{12} + 4c_{44}), \quad (2.37)$$

$$D = 18(c_{11} + c_{12} + 2c_{44}), \quad (2.38)$$

and variables with superscripts (i) and (ii) denote parameters specific to the core and shell materials, respectively.

In zinc blende structures the tangential and longitudinal lattice strain boundary conditions in the core and the shell are given by

$$f_t^{(i)} = \frac{a - a^{(i)}}{a^{(i)}}, \quad (2.39)$$

$$f_t^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}}, \quad (2.40)$$

$$f_l^{(i)} = \frac{a - a^{(i)}}{a^{(i)}}, \quad (2.41)$$

$$f_l^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}}, \quad (2.42)$$

where a represents the strained cubic lattice constant of the system, $a^{(i)}$ represents the unstrained lattice parameter of the core material and $a^{(ii)}$ represents the unstrained lattice parameter of the shell material. For a given geometry and material composition the equilibrium lattice constant, a , will assume a value that minimizes the total strain energy of the system. By minimizing $U_{strain} = U^{(i)} + U^{(ii)}$, the equilibrium lattice strain is found to be

$$a = \frac{a^{(ii)} a^{(i)} (a^{(ii)} r^2 \chi^{(i)} + a^{(i)} h (h + 2r) \chi^{(ii)})}{a^{(ii)2} r^2 \chi^{(i)} + a^{(i)} h (h + 2r) \chi^{(ii)}}, \quad (2.43)$$

where $\chi^{(i)}$ and $\chi^{(ii)}$ are given by

$$\chi_{\text{zinc blende}} = \frac{(c_{11} + 2c_{12})(c_{11} - c_{12} + 6c_{44})}{2(c_{11} + c_{12} + 2c_{44})}. \quad (2.44)$$

The equilibrium lattice constant value falls somewhere between the relaxed core and shell values, and will tend toward that of the region with greater volume. This is expected given the direct relationship between strain energy and volume seen in Eqs. (2.33) and (2.34). This result shows that for a given choice of material, geometry will determine the distribution of lattice strain between the core and shell materials. It is because of this that the dimensions of both core and shell must be considered in determining stable coherent geometries.

2.2.2 Partial Relaxation Through Dislocation Formation

The insertion of an edge dislocation at the core-shell interface can allow partial relaxation of lattice mismatch strain, but will also contribute a strain field associated with the dislocation itself. In order to determine the energetics associated with these phenomena it is necessary to identify the types of dislocations that are likely to form. This is done by first considering dislocations that are known to be stable in a given crystal structure, and from them, selecting those dislocations that will relieve lattice mismatch strain in the coaxial nanowire geometry.

2.2.2.1 Relaxation in Wurtzite Nanowires

The two types of dislocations considered for the wurtzite [0001] structure are shown in Figure 2.7. A pure edge dislocation along the [0001] direction with Burgers vector in the $\langle 11\bar{2}0 \rangle$, as shown in Figure 2.7(a), is expected to be stable and relieve strain in the cross section of the nanowire. Such dislocations have been observed in planar nitride films.⁴⁵ The strain energy associated with this type of dislocation is⁴⁶

$$U_{line} = n_{line} 2\pi r L \left(\frac{c_{11}^{(ii)} - c_{12}^{(ii)}}{2c_{11}^{(ii)}} \right) \frac{b_{line}^2}{4\pi} \log \left(\frac{4h}{b_{line}} \right), \quad (2.45)$$

where n_{line} refers to the dislocation line density per unit length about the circumference of the heterointerface and b_{line} refers to the magnitude of the Burgers vector for such a dislocation. In this expression the dislocation is assumed to be located at the heterointerface, as shown in Figure 2.7(a), and the strain field is assumed to terminate at the free surface of the nanowire system. Although the strain field generated by the

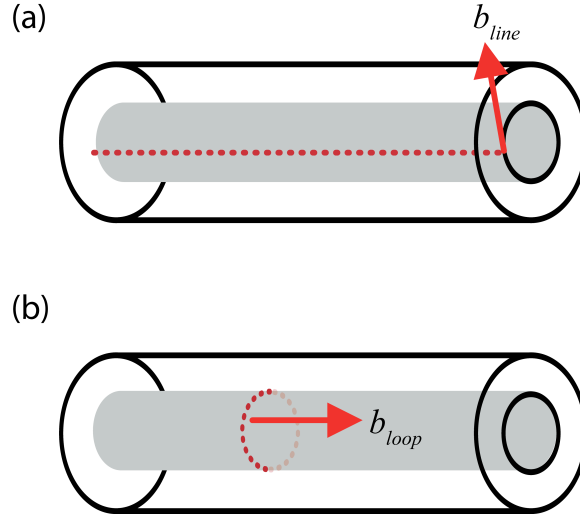


Figure 2.7

(a) Orientation of an edge dislocation line along the axis of the wire with a Burgers vector, b_{line} , tangential to the circular heterointerface. (b) Orientation of an edge dislocation loop in the cross-sectional plane of the wire with Burgers vector, b_{loop} , along the length of the wire.

dislocation will exist in both the core and shell materials, c_{ij} values are arbitrarily chosen to be those for the shell; this is reasonable since in most viable heterojunction material systems $c_{ij}^{(i)}$ and $c_{ij}^{(ii)}$ are sufficiently similar that the choice between them will not significantly impact the final calculation. The magnitude of b_{line} is expected to be that of the equilibrium lattice constant a .⁴⁷

Stable dislocations with Burgers vectors in the $[0001]$ direction can also form in the wurtzite crystal structure.⁴⁶ If an edge dislocation loop with such a Burgers vector should form around the core, as shown in Figure 2.7(b), some longitudinal strain in the wire would be relieved. Given that edge dislocations with such a Burgers vector are not observed in the planar case, we do not expect these dislocations to play

a major role in coaxial structures but include it for completeness. The strain energy associated with such a dislocation loop is⁴⁶

$$U_{loop} = n_{loop} L 2\pi r \left(c_{13}^{(ii)} + \sqrt{c_{11}^{(ii)} c_{33}^{(ii)}} \right) \sqrt{\frac{c_{44}^{(ii)} \left(\sqrt{c_{11}^{(ii)} c_{33}^{(ii)}} - c_{13}^{(ii)} \right)}{c_{11}^{(ii)} \left(c_{13}^{(ii)} + 2c_{44}^{(ii)} + \sqrt{c_{11}^{(ii)} c_{33}^{(ii)}} \right)}}} \times \frac{b_{loop}^2}{4\pi} \log \left(\frac{32r}{b_{loop}} - 1 \right), \quad (2.46)$$

where n_{loop} refers to the dislocation loop density per unit length along the z axis of the wire and b_{loop} refers to the magnitude of the Burgers vector, which is assumed to be that of the equilibrium lattice constant c .

In examining the energetics of a dislocation at the interface it is necessary to consider not only the strain field associated with the dislocation itself, but also the lattice relaxation that is expected to occur with the inclusion of a dislocation. For planar thin films grown on bulk substrates, the one-dimensional lattice strain including relaxation due to dislocation formation, is given by⁵

$$f_{film} = \frac{a_{substrate} - a_{film}}{a_{film}} - n b, \quad (2.47)$$

where $a_{substrate}$ represents the strained lattice constant of the film, a_{film} represents the relaxed lattice constant of the film, n refers to the line dislocation density per unit length and b refers to the edge component of the dislocation Burgers vector. The lattice relaxation term $n b$ accounts for the film relaxation due to the formation of dislocations at the heterointerface. The system described by Eq. (2.47) assumes all strain will be in the film, and thus only relaxation in the film is considered.

In the case of the coaxial nanowire structures, strain will be distributed between the core and the shell. The formation of an edge dislocation at the interface will result in the insertion of an extra plane of atoms in the system. This will change the strain constraint in both core and shell materials since the two are interdependent. Because the system will tend to minimize total strain energy, the more heavily strained material will receive the bulk of the lattice relaxation that occurs. It is therefore necessary to distribute the lattice relaxation term between the core and shell while incorporating it into the lattice strain expressions. The resulting strain expressions are then

$$f_t^{(i)} = \frac{a - a^{(i)}}{a^{(i)}} - \left(\frac{a^{(i)} - a}{|a^{(i)} - a^{(ii)}|} \right) n_{line} b_{line} , \quad (2.48)$$

$$f_t^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}} - \left(\frac{a - a^{(ii)}}{|a^{(i)} - a^{(ii)}|} \right) n_{line} b_{line} , \quad (2.49)$$

$$f_l^{(i)} = \frac{c - c^{(i)}}{c^{(i)}} - \left(\frac{c^{(i)} - c}{|c^{(i)} - c^{(ii)}|} \right) n_{loop} b_{loop} , \quad (2.50)$$

$$f_l^{(ii)} = \frac{c - c^{(ii)}}{c^{(ii)}} - \left(\frac{c - c^{(ii)}}{|c^{(i)} - c^{(ii)}|} \right) n_{loop} b_{loop} . \quad (2.51)$$

These expressions resemble Eq. (2.47) except that the lattice relaxation term is now divided between the core and shell. Eqs. (2.48)-(2.51) model the effect described earlier by using the equilibrium lattice constant and the relaxed lattice constant values to apportion the relaxation term according to the relative amounts of strain present in the core and shell materials. Numerical computations were carried out by applying

values from a number of specific cases to then minimize the total energy in the system with respect to the division of the strain relaxation term. The results of these calculations were found to be nearly identical to the functions used in Eqs. (2.48)-(2.51), confirming that the equilibrium lattice constant can be used to estimate the distribution of strain relaxation between the core and shell.

2.2.2.2 Relaxation in Zinc Blende Nanowires

Dislocations in zinc blende structures tend to be either pure screw or 60° mixed dislocations along the $\langle 011 \rangle$ directions.⁴⁶ For zinc blende nanowires grown along the $[111]$ direction, it is not possible for a perfect edge dislocation to lie along the length of the nanowire as shown in Figure 2.7(a). Thus this type of dislocation is not expected to define the critical dimensions in zinc blende structures.

The formation of a dislocation loop around the core of the nanowire, as shown in Figure 2.7(b), could serve to relieve lattice strain along the length of the wire and has been observed in some coaxial nanowires heterostructures with zinc blende regions.⁴⁸ Such an edge dislocation loop could form as a result of a partial-stacking fault. Zinc blende wires oriented in the $[111]$ direction are comprised of (111) planes of atoms stacked in an ABC sequence, as shown in figure 2.8(a). A stacking fault will either insert or remove a (111) plane of atoms in the core or shell of the structure, as shown in figure 2.8(b). This insertion or removal of a (111) plane will result in a two dimensional dislocation in the region where the stacking fault has occurred, but will also create an edge dislocation loop⁴⁶ around the core region of the

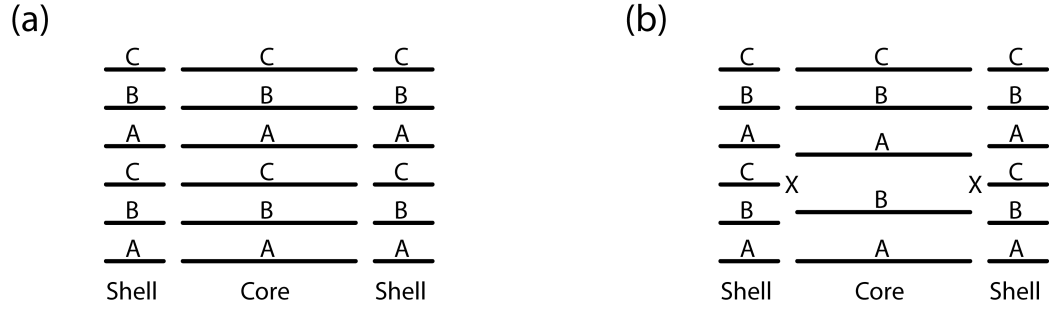


Figure 2.8

(a) Stacking sequence of (111) planes in a coherently strained [111] zinc blende coaxial nanowire. (b) Stacking sequence of (111) planes in a [111] zinc blende nanowire with a stacking fault in the core region. The 'X' represents the location of an edge dislocation loop formed around the core as a result of the stacking error.

heterostructure, such as the one shown in Figure 2.7(b). The magnitude and orientation of the Burgers vector of such a loop will efficiently relieve longitudinal strain and is thus expected to be the type of dislocation that will define the critical dimensions in zinc blende coaxial heterostructures.

When calculating the energy associated with such a dislocation it is necessary to consider the strain energy associated with the partial edge dislocation loop about the core as well as the energy due to the stacking fault. The total energy associated with this type of dislocation is⁴⁶

$$U_{loop} = n_{loop} L \left(2\pi r \frac{1}{6} (c_{11}^{(ii)} - c_{12}^{(ii)} + 4c_{44}^{(ii)}) \frac{b_{loop}^2}{4\pi} \log \left[\frac{32r}{b_{loop}} - 1 \right] + \gamma A_{fault} \right) \quad (2.52)$$

where n_{loop} refers to the dislocation loop density per unit length along the axis of the wire, b_{loop} refers to the magnitude of the Burgers vector, γ is the stacking fault energy per unit area and A_{fault} is the area of the stacking fault. Although the strain field

generated by the dislocation will exist in both the core and shell materials, c_{ij} values are arbitrarily chosen to be those of the shell; this is reasonable since in most viable heterojunction material systems $c_{ij}^{(i)}$ and $c_{ij}^{(ii)}$ are sufficiently similar that the choice between them will not significantly impact the final calculation. The value of b_{loop} is expected to be $a/\sqrt{3}$ for this type of dislocation⁴⁶ and A_{fault} will be the cross-sectional area of the core or the shell depending on the region in which the stacking error has occurred. It should be noted that Eq. (2.52) is derived for a dislocation loop in an infinite medium, but because the expression assumes that the loop terminates its own strain field, it should produce a reasonable estimate for the strain energy in sufficiently large coaxial nanowire structures.

In examining the energetics of a dislocation at the interface it is necessary to consider not only the strain energy associated with the dislocation itself, but also the lattice relaxation that is expected to occur with the inclusion of a dislocation. For planar thin films grown on bulk substrates, the one-dimensional lattice strain including relaxation due to dislocation formation, is given by Eq. (2.47).

As in the case for wurtzite coaxial nanowire structures, strain in zinc blende coaxial nanowires will also be distributed between the core and the shell. The formation of an edge dislocation at the interface will result in the insertion or removal of a plane of atoms in the system. This will change the strain constraint in both core and shell materials since the two are interdependent. Because the system will tend to minimize total strain energy in the system, the region experiencing the greater lattice mismatch will receive the bulk of the lattice relaxation that occurs. It is therefore

necessary to distribute the lattice relaxation term between the core and shell while incorporating it into the lattice strain expressions. The lattice mismatch strain expressions are then given by

$$f_l^{(i)} = \frac{a - a^{(i)}}{a^{(i)}} - \left(\frac{a^{(i)} - a}{|a^{(i)} - a^{(ii)}|} \right) n_{loop} b_{loop}, \quad (2.53)$$

$$f_l^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}} - \left(\frac{a - a^{(ii)}}{|a^{(i)} - a^{(ii)}|} \right) n_{loop} b_{loop}, \quad (2.54)$$

These expressions resemble Eq. (2.47) except that the lattice relaxation term is now divided between the core and shell. Eqs. (2.53) and (2.54) model the effect described above by using the equilibrium lattice constant and the relaxed lattice constant values to apportion the relaxation term such that the total strain energy in the system is minimized. Numerical computations were carried out to minimize the total energy in the system with respect to the division of the strain relaxation term. The results of these calculations were found to be nearly identical to the functions used in Eqs. (2.53)-(2.54), confirming that the equilibrium lattice constant can be used to estimate the distribution of strain relaxation between the core and shell.

2.2.3 Critical Geometry Calculation

The total strain energy in the system is the sum of the lattice mismatch strain energy in the core and shell regions as well as the energy due to the presence of the dislocations discussed above. The expressions for the total strain energy for zinc blende and wurtzite structures including dislocations are

$$U_{tot} = U_{ZB}^{(i)} + U_{ZB}^{(ii)} + U_{loop}, \quad (2.55)$$

$$U_{tot} = U_W^{(i)} + U_W^{(ii)} + U_{line} + U_{loop}, \quad (2.56)$$

respectively, where $U_{ZB}^{(i)}$ and $U_{ZB}^{(ii)}$ are calculated using Eqs. (2.48)-(2.51) and where $U_W^{(i)}$ and $U_W^{(ii)}$ are calculated using Eqs. (2.39)-(2.40) and Eqs. (2.53)-(2.54). The critical dimensions are obtained by determining the geometric limits at which it becomes energetically favorable to include a dislocation. This is done mathematically by evaluating $\partial U_{tot} / \partial n|_{n=0}$ and determining the dimensions for which this function changes from positive to negative.⁵

Such an analysis will determine the dimensions at which sufficient strain energy will be relieved by the insertion of a single dislocation to make up for the energy cost of inserting the dislocation. However it does not take into account the energetic effects of interactions between dislocations, which are expected to be significant for nanoscale structures, and thus is only valid at the critical dimensions at which the first dislocation forms.

2.3 Results and Discussion

Figure 2.9 shows a schematic plot indicating the general form of the results of the critical dimension calculation obtained for a specific wurtzite and zinc blende structure. The shaded portions of the plots show the combinations of core-shell dimensions that will yield coherently strained structures for a particular choice of

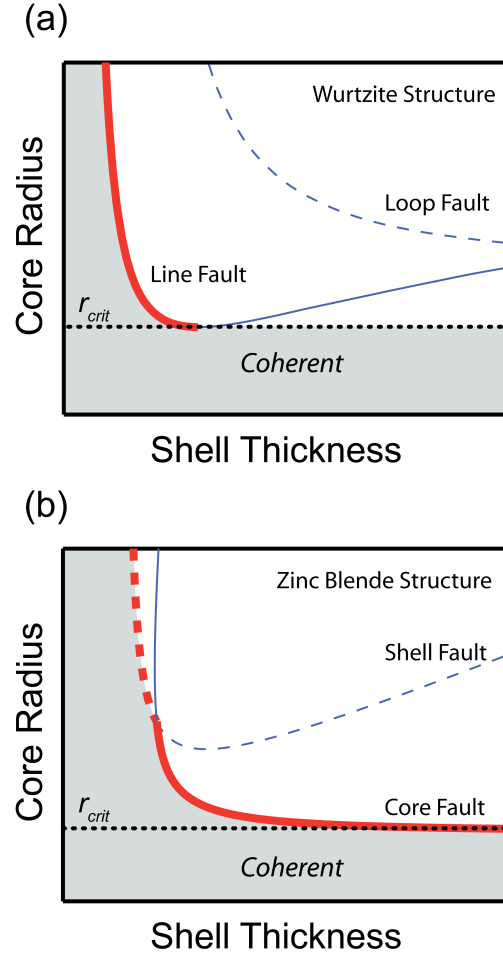


Figure 2.9

Schematic plot of the critical dimensions for a (a) wurtzite and (b) zinc blende coaxial nanowire structure. The shaded region of the plots show all possible strained coherent geometries, which are quantified by the critical core radius r_{crit} and the critical shell thickness curve (thick red portion of the curves).

material and alloy composition. More detailed calculation results for specific structures will be shown in Figures 2.10-2.12.

The curves in Figure 2.9 show the limiting geometries for dislocation formation. The solid and dashed curves in Figure 2.9(a) shows the limiting dimensions for the formation of a dislocation line and loop in a wurtzite nanowire, respectively.

The solid and dashed curves in figure 2.9(b) show the limiting dimensions for the formation of a stacking fault in the core and shell regions of a zinc blende nanowire, respectively. From Figures 2.9(a) and 2.9(b) we see that for a given combination of materials forming the coaxial nanowire heterostructure, there is a critical core radius, r_{crit} , below which the coaxial nanowire will be coherent regardless of shell thickness. Such a critical core radius exists because of the coaxial nanowire structure's ability to distribute strain between the core and shell. As the shell thickness increases eventually all of the strain is passed to the core. Since the core volume is constant, the strain energy of the system will no longer change with shell thickness. If the core volume is sufficiently small then the strain energy stored in the core will never be great enough to warrant the formation of a dislocation.

The thicker red portion of the line fault curve in Figure 2.9(a) defines a critical shell thickness for wurtzite structures with core radius larger than the critical core radius value. This critical shell thickness represents the shell thickness value at which it becomes energetically favorable to insert a line dislocation at the heterointerface for a given core radius. The placement of the loop fault curve above the line fault curve suggests that coherence will always be lost through the formation of a line dislocation along the length of the nanowire. The positively sloped region of the line dislocation curve (lighter blue portion of the curve) is a function of the assumption, used to calculate the dislocation strain energy, U_{line} , that no other dislocations are present to terminate the dislocation strain field. Because a dislocation must have already formed

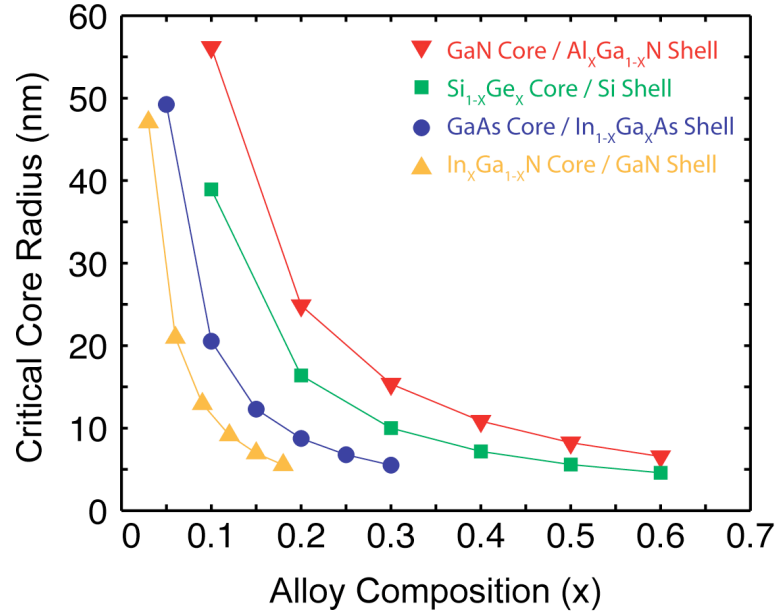


Figure 2.10

Plot of the critical core radius for various nanowire heterostructures as a function of alloy composition. The structures considered are comprised of an InAs core with an In_{1-x}Ga_xAs shell (●), Si_{1-x}Ge_x core with a Si shell (■), GaN core with an Al_xGa_{1-x}N shell (▼), and In_xGa_{1-x}N core with a GaN shell (▲).

in order to arrive at this region on the plot the features of the curve in this region are not applicable in determining coherence.

The thicker red portions of the curves in Figure 2.9(b) define a critical shell thickness for zinc blende structures with a core radius larger than the critical core radius. This critical shell thickness represents the shell thickness at which it becomes energetically favorable for a stacking fault to form. From Figure 2.9(b) it is clear that at core radius values close to r_{crit} the critical shell thickness will be limited by the formation of a stacking fault in the core region. As the core radius increases, however, the coherence limit will be defined by the formation of a stacking fault in the shell region. This occurs because the energy associated with a stacking fault in the core

region increases more rapidly with core radius than the energy associated with a stacking fault in the shell region. Though the mechanisms by which coherency is lost differ between zinc blende and wurtzite structures, Figure 2.9 shows that in both cases the critical dimensions can be quantified by a critical core radius below which dislocations will never form, and a critical shell thickness that is dependent on core radius.

Numerical calculations were carried out for a number of material systems as a function of alloy composition. Figure 2.10 shows the calculated critical core radii as a function of alloy composition for wurtzite structures comprised of GaN cores with $\text{Al}_x\text{Ga}_{1-x}\text{N}$ shells and $\text{In}_x\text{Ga}_{1-x}\text{N}$ cores with GaN shells, as well as zinc blende structures comprised of $\text{Si}_{x-1}\text{Ge}_x$ cores with Si shells and InAs cores with $\text{In}_{x-1}\text{Ga}_x\text{As}$ shells. Figures 2.11(a), 2.11(b), 2.12(a) and 2.12(b) show the calculated critical dimensions for these structures, respectively. Each curve in Figures 2.11 and 2.12 plots the combination of core radius and shell thickness at which the first dislocation is expected to form for a given alloy composition. Figures 2.10, 2.11 and 2.12 were calculated using the material parameter values^{44,49,50} listed in Tables 2.1 and 2.2, all of which were assumed to vary linearly with alloy composition. Figures 2.10, 2.11 and 2.12 suggest that the critical dimensions for reasonable alloy compositions are well within the range of experimental interest. In general these results show that there are a variety of compositional and geometric choices that will yield coherent structures, giving device designers a flexibility that is typically not observed in planar thin film devices.

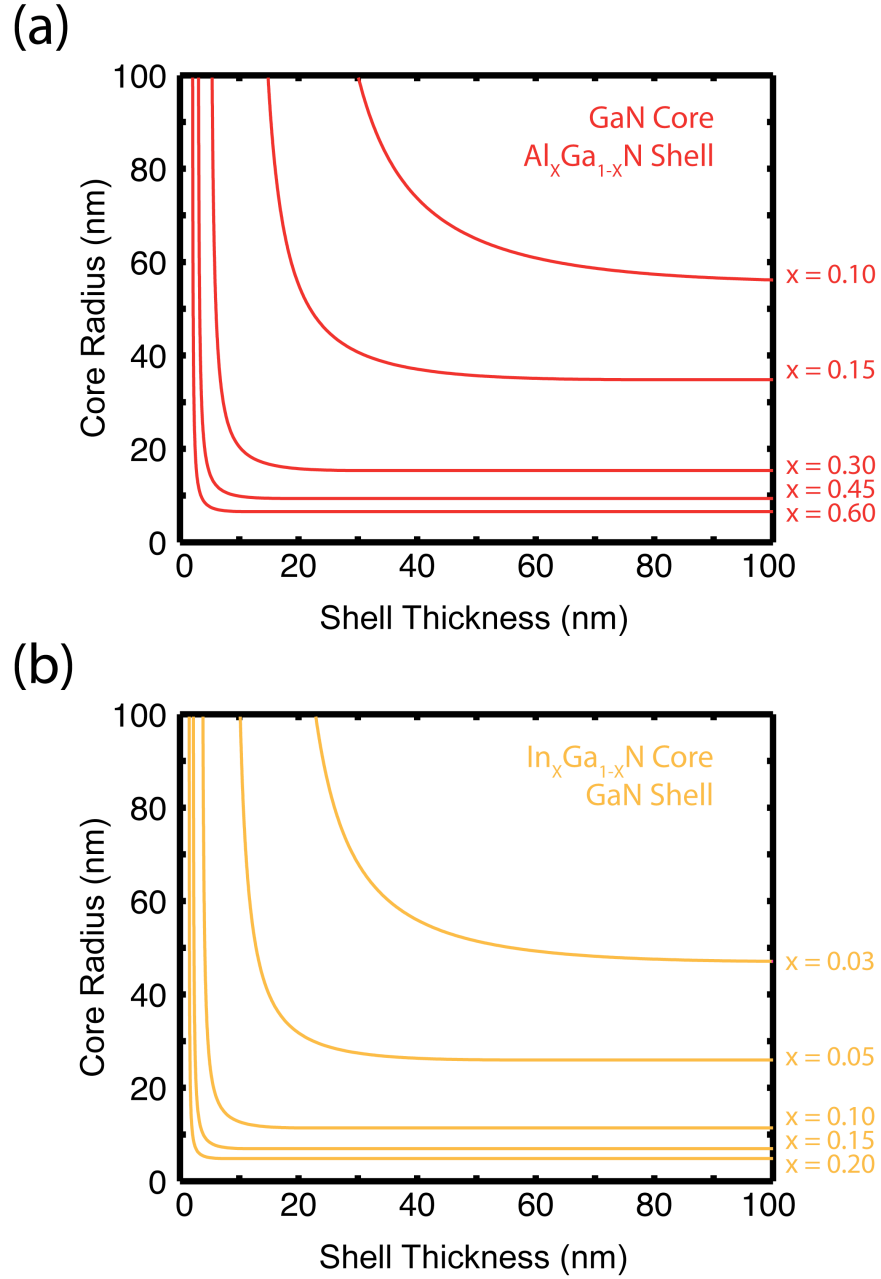


Figure 2.11

Critical dimensions for various wurtzite nanowire heterojunctions comprised of (a) GaN cores with $\text{Al}_x\text{Ga}_{1-x}\text{N}$ shells and (b) $\text{In}_x\text{Ga}_{1-x}\text{N}$ core with GaN shells.

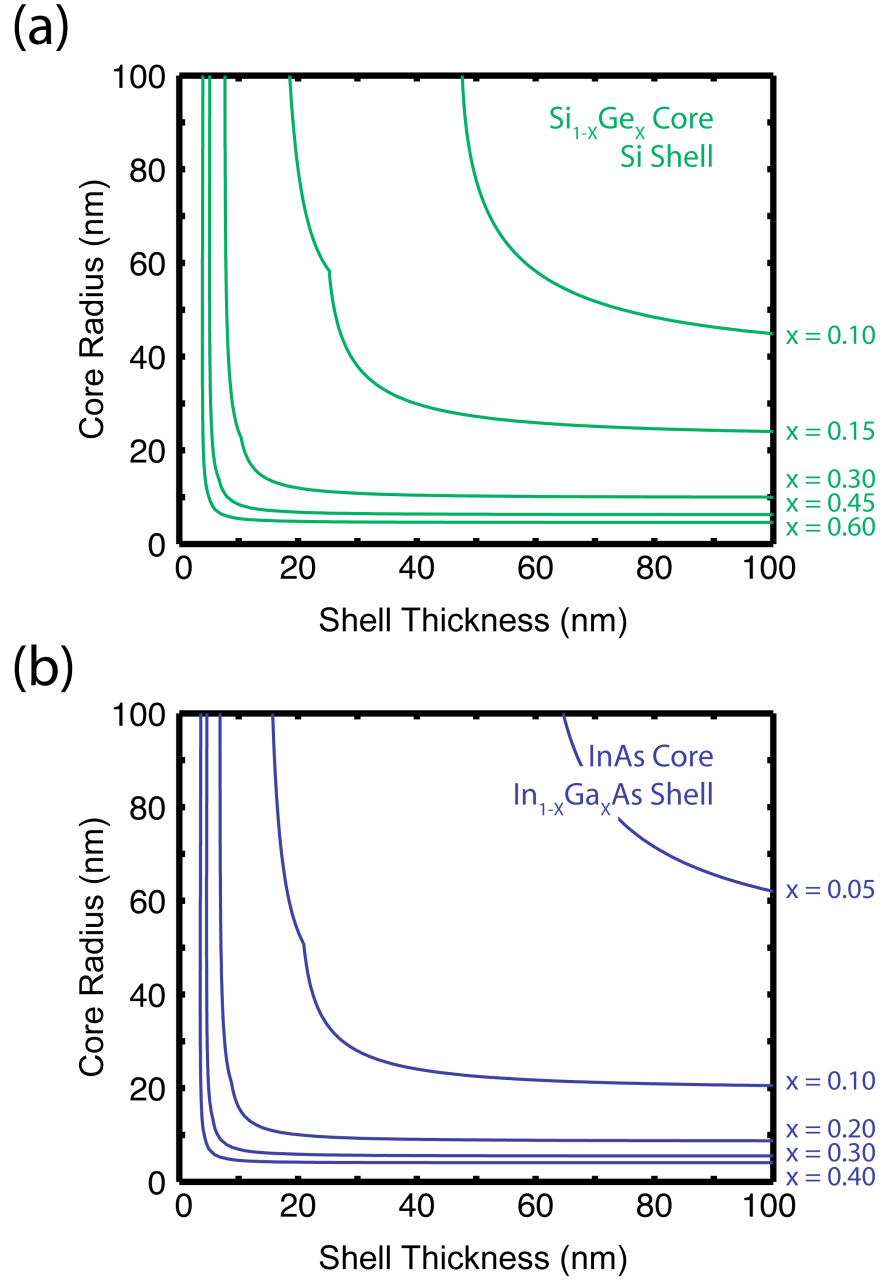


Figure 2.12

Critical dimensions for various zinc blende nanowire heterojunctions comprised of (a) $\text{Si}_{1-x}\text{Ge}_x$ cores with Si shells and (b) InAs cores with $\text{In}_{1-x}\text{Ga}_x\text{As}$ shells.

Table 2.1

Relevant physical parameters for wurtzite materials

	GaN	AlN	InN	Reference
a (Å)	3.199	3.110	3.585	44
c (Å)	5.227	4.995	5.801	44
c_{11} (GPa)	370	410	223	44
c_{12} (GPa)	145	140	115	44
c_{13} (GPa)	110	100	92	44
c_{33} (GPa)	390	390	224	44
c_{44} (GPa)	90	120	48	44

Table 2.2

Relevant physical parameters for zinc blende materials.

	InAs	GaAs	Si	Ge	Reference
a (Å)	6.0583	5.6533	5.4310	5.6580	49
c_{11} (GPa)	83	119	160	124	49
c_{12} (GPa)	45	54	58	41	49
c_{44} (GPa)	40	60	80	68	49
γ (mJ/m ²)	30	45	55	60	50

2.4 Conclusions

Few structures such as these have been fabricated and accurately characterized for alloy composition and/or the presence of dislocations. As result limited data exists in the literature to directly determine the validity of this model. In examining the dimensions of core-shell structures that have been fabricated into devices,^{9,26-32} however, it seems that the model does hold predictive value in determining core-shell structures that are appropriate for device applications.

By increasing the core radius of a wurtzite nanowire, the critical dimension calculation is shown to approach the well-known theoretical calculation for planar thin films,⁵¹⁻⁵³ confirming that this model is consistent with accepted methods to determine critical thickness in thin film structures. For the zinc blende nanowire critical dimension formalism such a comparison is not possible. This is because the geometry of the zinc blende nanowire heterostructure suggests relaxation will occur through the formation of a dislocation loop with a self-terminating strain field. Increasing the radius of this type of dislocation will not simplify into a line dislocation due to inherent assumptions made within the expression for the strain field for these types of dislocations. As core radius in this type of nanowire is increased it is expected that it will start behaving more like a planar system and relax through the formation of 60° mixed dislocations along the $\langle 011 \rangle$ directions rather than a stacking fault thus invalidating this model.

In summary, we have utilized a methodology, based on the well-known formalism used to determine the critical thickness in planar epitaxial growth, to determine coherent geometries for various zinc blende and wurtzite coaxial nanowire heterostructures. The unique geometry of the nanowire structure along with the volumetric similarity of the materials involved give rise to a number possible coherent structures for a given choice of materials and alloy compositions, which are quantified by a unique critical core radius and a critical shell thickness that is a function of the core radius. This flexibility is unique to nanowire structures and provides material and device engineers with increased flexibility in design not available in planar thin film heterostructures.

Portions of this chapter have been published in Journal of Applied Physics, 2006, S. Raychaudhuri and E. T. Yu. The dissertation author is the first author of this paper.

Portions of this chapter have been published in Journal of Vacuum Science and Technology B, 2006, S. Raychaudhuri and E. T. Yu. The dissertation author is the first author of this paper.

References

- ¹ <http://www.veeco.com/images/library/Nitrides2b.jpg>
- ² J.W. Matthews and A. E. Blakeslee, *J. of Cryst. Growth*, **27**, 118 (1974).
- ³ J.W. Matthews, *J. Vac. Sci. Technol.*, **12**, 126 (1975).
- ⁴ C.A.B. Ball and J. H. van der Merwe, “The growth of dislocation-free layers” in Dislocations in Solids, Chap. 27, F. R. N. Nabarro, Ed., North Holland, Amsterdam (1983).
- ⁵ J. Y. Tsao, Materials Fundamentals of Molecular Beam Epitaxy, Academic Press, San Diego, pp. 151-168 (1993).
- ⁶ M. Law, J. Goldberger, and P. Yang, *Annu. Rev Mater. Res.*, **34**, 83 (2004).
- ⁷ W. Lu and C. M. Lieber, *J. Phys. D: Appl. Phys.*, **39**, R387 (2006).
- ⁸ M. T. Björk, B. J. Ohlsson, C. Thelander, A. I. Persson, K. Deppert, L. R. Wallenberg, and L. Samuelson, *Appl. Phys. Lett.*, **81**, 4458 (2002).
- ⁹ J. Xiang, W. Lu, Y. Hu, Y. Wu, H. Yan, and C. M. Lieber, *Nature*, **441**, 489 (2006).
- ¹⁰ M. T. Björk, O. Hayden, H. Schmid, H. Riel and W. Riess, *Appl. Phys. Lett.*, **90**, 142110 (2007).
- ¹¹ S. A. Dayeh, C. Soci, P. K. L. Yu, E. T. Yu,a and D. Wang, *Appl. Phys. Lett.*, **90**, 162112 (2007).
- ¹² Y. Hu, J. Xiang, G. Liang, H. Yan, C. M. Lieber, *Nano Lett.*, **8**, 925 (2008).
- ¹³ C. Thelander, L. E. Fröberg, C. Rehnstedt, L Samuelson, and L.-E. Wernersson, *Elect. Dev. Lett.*, **29**, 206 (2008).
- ¹⁴ P. J. Pauzauskie and P. Yang, *Materials Today*, **10**, 36, (2006).
- ¹⁵ F. Qian, S. Gradecak, Y. Li, C.-Y. Wen, and C. M. Lieber, *Nano Lett.*, **5**, 2287 (2005).
- ¹⁶ F. Qian, Y Li, S Gradecak, H.-G. Park, Y. Dong, Y Ding, Z. L. Wang and C. M. Lieber, *Nature Materials*, **7**, 701 (2008).

-
- ¹⁷ C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, J. Park, X.Y. Bao, YH. Lo, D. Wang, *Nano Lett.*, **7**, 1003 (2007).
- ¹⁸ C. J. Novotny, E. T. Yu, and P. K. L. Yu, *Nano Lett.*, **8**, 775 (2008).
- ¹⁹ Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science*, **293**, 1289 (2001).
- ²⁰ M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, *Angew. Chem. Int. Ed.*, **41**, 2405 (2002).
- ²¹ Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, *Nano Lett.*, **4**, 245 (2004).
- ²² M. C. McApline, H. Ahmad, D. Wang and J. R. Heath, *Nature Materials*, **6**, 379 (2007).
- ²³ F. Patolsky, B. P. Timko, G. Zheng, and C. M. Lieber, *MRS Bulletin*, **32**, 142 (2007).
- ²⁴ F. Patolsky, B. P. Timko, G. Yu, Y. Fang, A. B. Greytak, G. Zheng, and C. M. Lieber, *Science*, **313**, 1100 (2006).
- ²⁵ W. Kim, J. K. Ng, M. E. Kunitake, B. R. Conklin, and P. Yang, *J. A. Chem. Soc.*, **129**, 7228 (2007).
- ²⁶ L. J. Lauhon, M. S. Gudiksen, D. Wang, and C. M. Lieber, *Nature*, **420**, 57 (2002).
- ²⁷ W. Lu, J. Xiang, B. P. Timko, Y. Wu, and C. M. Lieber, *Proc. Natl. Acad. Sci. USA*, **102**, 10046 (2005).
- ²⁸ Z. Zanolli, L. E. Fröberg, M. T. Björk, M.-E. Pistol, and L. Samuelson, *Thin Film Solids*, **515**, 793 (2006).
- ²⁹ X. Jiang, A. Vidan, M. Tinkhan, R. M. Westervelt, and C. M. Lieber, *Nature Nanotechnology*, **1**, 208 (2006).
- ³⁰ X. Jiang, Q. Xiong, S. Nam, F. Qian, Y. Li, and C. M. Lieber, *Nano Lett.*, **7**, 3214 (2007).
- ³¹ H.-Y. Li, O. Wunnicke, M. T. Borgström, W. G. G. Immink, M. H. M. Van Weert, M. A. Verheijen, and E. P. A. M. Bakkers, *Nano Lett.*, **7**, 1144 (2007).
- ³² Y. Hu, H. O. H. Churchill, D. J. Reilly, J. Xiang, C. M. Lieber, and C. M. Marcus, *Nature Nanotechnology*, **2**, 622 (2007).

-
- ³³ Y. Wu, R. Fan, and P. Yang, *Nano Lett.*, **2**, 83 (2002).
- ³⁴ K. A. Dick, S. Kodambaka, M. C. Reuter, K. Deppert, L. Samuelson, W. Seifert, L. R. Wallenberg, and F. M. Ross, *Nano Lett.*, **7**, 1817 (2007).
- ³⁵ M. Paladugu, J. Zou, Y.-N. Guo, G. J. Auchterlonie, H. J. Joyce, Q. Gao, H. H. Tan, C. Jagadish, Y. Kim, *Small*, **3**, 1873 (2007).
- ³⁶ M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith and C. M. Lieber, *Nature*, **415**, 617 (2002).
- ³⁷ M. Y. Gutkin, I. A. Ovid'ko and A. G. Sheinerman, *J. Phys.: Condens. Matter*, **12**, 5391 (2000).
- ³⁸ Y. Liang, W. D. Nix, P. B. Griffin and J. D. Plummer, *J. Appl. Phys.*, **97**, 043519 (2005).
- ³⁹ K. E. Aifantis, A. L. Kolesnikova, A. E. Romanov *Philosophical Magazine*, **87**, 4731 (2007).
- ⁴⁰ E. Ertekin, P. A. Greaney, D. C. Chrzan and T. D. Sands, *J. Appl. Phys.*, **97**, 114325 (2005).
- ⁴¹ F. Glas, *Phys. Rev. B*, **74**, 121302 (2006).
- ⁴² S. Raychaudhuri and E. T. Yu, *J. Appl. Phys.*, **99**, 114308 (2006).
- ⁴³ J.F. Nye, Physical Properties of Crystals, (Oxford University Press, Oxford, 1985) pp. 82-104, 131-142.
- ⁴⁴ O. Ambacher, J. Majewski, C. Miskys, A. Link, M. Hermann, M. Eickhoff, M. Stutzmann, F. Bernardini, V. Fiorentini, V. Tilak, B. Schaff and L. F. Eastman, *J. Phys.: Condens. Matter*, **14**, 3399 (2002).
- ⁴⁵ P. Cantu, F. Wu, P. Waltereit, S. Keller, A. E. Romanov, S. P. DenBaars and J. S. Speck, *J. Appl. Phys.*, **97**, p. 103534 (2005).
- ⁴⁶ John Price Hirth and Jens Lothe, Theory of Dislocations, (McGraw-Hill Book Company, New York, 1968), pp. 29-56, 140-144, 254-265, 288-307, 355-562, 411-432

-
- ⁴⁷ J. A. Floro, D. M. Follstaedt, P. Provencio, S. J. Hearne, and S. R. Lee, *J. Appl. Phys.*, **96**, p. 7087, (2004).
- ⁴⁸ H.-M. Lin, Y.-L. Chen, J. Yang, Y.-C. Liu, K.-M. Yin, J.-J. Kai, F.-R. Chen, L.-C. Chen, Y.-F. Chen, and C.-C. Chen, *Nano Lett.*, **3**, p. 537 (2003)
- ⁴⁹ Landolt-Börnstein - Group III Condensed Matter, Volume 41, Issue 1, Jan 2001
- ⁵⁰ S. Takeuchi and K. Suzuki, *Phys. Status Solidi A* **171**, p.99 (1999)
- ⁵¹ S. R. Lee, D. D. Koleske, K. C. Cross, J. A. Floro, K. E. Waldrip, A. T. Wise and S. Mahajan, *Appl. Phys. Lett.* **85**, p. 6164 (2004).
- ⁵² A. D. Bykhovski, B. L. Gelmont, and M. S. Shur, *J. Appl. Phys.* **81**, p. 6332 (1997).
- ⁵³ A. D. Bykhovski, B. L. Gelmont, and M. S. Shur, *J. Appl. Phys.* **78**, p. 3691 (1995).

Chapter 3

Dielectrophoretic Nanowire Integration

3.1 Introduction

As outlined in Chapter 1, successes in the growth and fabrication of semiconductor nanowires^{1,2} have led to new opportunities in novel device design for applications in electronics,³⁻⁸ optoelectronics,⁹⁻¹³ sensing¹⁴⁻¹⁷ and biology.¹⁸⁻²⁰ While many individual nanowire devices have been demonstrated, there are very few examples of large (or moderately sized) nanowire systems. Manipulating and placing nanowires in a coherent and useful fashion continues to be a considerable challenge. A number of schemes have been proposed to meet this challenge and include fluidic assembly,²¹⁻²³ Langmuir-Blodgett films,²⁴⁻²⁷ template based assembly²⁸⁻³⁴ and dielectrophoresis (DEP).³⁵ While Langmuir-Blodgett techniques and fluidic assembly offer the ability to line up nanowires in parallel, they offer little control over where nanowires will finally end up on a substrate making it difficult to interface individual wires with a larger system. Template based assembly utilizes nanoimprint lithography or e-beam lithography to define patterns that can then allow for coherently fabricated nanowires. This allows for greater control over the nanowire placement relative to each other as well as a larger system, but often limits the way in which a wire can be fabricated requiring specific materials or device structures and thus may not allow

for more advanced geometries such as axial or coaxial heterojunctions.

Dielectrophoresis (DEP) refers to the use of electric fields to manipulate neutrally charged particles in solution³⁶⁻³⁸ and can be used to attract nanowires (suspended in solution) onto predefined electrodes.³⁵ DEP offers the ability to assemble a wide variety of nanowires and is not limited by the way in which a nanowire is fabricated. It can be tailored to work with nanowires of various conductivities and materials. Furthermore, because the nanowires are placed on predefined electrodes, identifying their final location and thus integrating them with a larger system becomes trivial. DEP also allows the added flexibility of integrating several different types of nanowires into one system by performing a series of DEP steps. In order to fully realize these capabilities DEP must be carefully controlled to ensure that wires are placed precisely at desired locations, and only at desired locations. To this end it is necessary to determine the relevant parameters that effect DEP and how to control them.

3.1.1 Dielectrophoresis

A charged particle, when placed in a uniform or non-uniform electric field, will be acted on by an electrostatic force that will move it along the electric field toward the electrode of opposite polarity. This is known as *electrophoresis*.³⁶ Similarly, an electrically neutral particle will also will also have a force exerted on it by an external field, but in this case the field must be non-uniform. This is referred to as *dielectrophoresis*. Dielectrophoresis can be defined as the force exerted on an

induced dipole in a neutral conducting or insulating particle due to the presence of a non-uniform, external electric field.³⁶⁻³⁸

The physical basis for dielectrophoresis is well established. The free and bound charges in a neutral particle will redistribute to form an effective dipole when that particle is placed in an external electric field. Because the particle is electrically neutral, each pole of the dipole is expected to have an equal and opposite charge (assuming the particle is isotropic). In a uniform electric field each equal and opposite pole of the dipole will be acted on by an identical electric field, resulting in equal and opposite electrostatic forces which will cancel each other out resulting in no net force on the particle. In a non-uniform electric field each equal and opposite pole of the dipole will be acted on by differing electric fields resulting in a net force causing the particle to move according to the gradient of the electric field. This is illustrated in Figure 3.1 where the negative pole of the dipole is in a larger gradient resulting in a net force on the particle toward the smaller electrode. Figure 3.1 illustrates DC dielectrophoresis where the polarity of each electrode is held constant. If the electrodes are driven by an AC potential the translational force on the neutrally charged particle will be the same, toward the smaller electrode, assuming the frequency of the AC potential is sufficiently low that the induced dipole is able to form. This is because the net force on the particle is dependent on the gradient of the electric field and not the polarity.

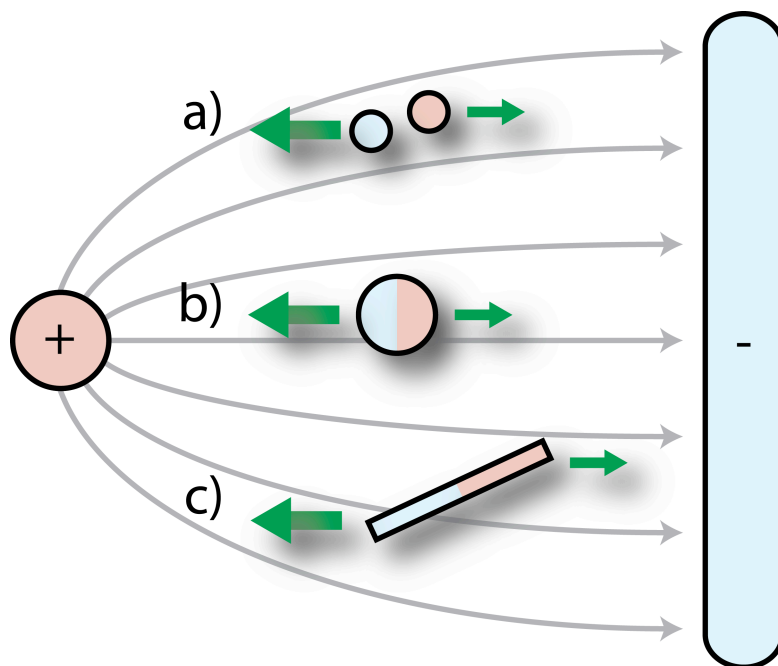


Figure 3.1

Schematic illustration of electrophoresis (a) and dielectrophoresis on a particle (b) and nanowire (c). Positive charge is represented in pink and negative charge is represented in blue. a) Electrostatic force on each charged particle will draw it toward the electrode of opposite polarity. b) A neutrally charged particle will form a dipole when placed in an external electric field. The field gradient results in a stronger electrostatic force on the negative pole of the particle resulting in a net translational force along the field gradient. c) In addition to the translational force felt by the nanowire, the mismatch in electrostatic force on the two poles in a nanowire will also result in a torque force which will align the nanowire axis along the electric field.

In addition to the translational dielectrophoretic force, particles with large aspect ratios, such as nanowires, will also be influenced by a dielectrophoretic torque force which will align the nanowire axis along the electric field.^{37,38} This is because the anisotropic shape of the nanowire will result in the strongest dipole moment along the long axis of the wire, whose most stable orientation will be parallel to the electric field.

The dielectrophoretic force on a particle can be calculated analytically.³⁶⁻³⁸

First, consider the force on a dipole in a non-uniform electric field, given by

$$\mathbf{F}_{\text{dipole}} = \mathbf{p} \cdot \nabla \mathbf{E}, \quad (3.1)$$

where $\mathbf{p}$ represents the dipole moment vector and $\mathbf{E}$ represents the electric field vector. In a time varying electric field this force equation becomes

$$\mathbf{F}_{\text{dipole}}(t) = \text{Re}[\mathbf{p}^* \exp(j\omega t)] \cdot \nabla \text{Re}[\mathbf{E}^* \exp(j\omega t)], \quad (3.2)$$

where $\mathbf{p}^*$ represents the complex dipole moment vector and $\mathbf{E}^*$ represents the complex electric field vector. From this expression it is possible to calculate the time-average force expression, given by

$$\langle \mathbf{F}_{\text{dipole}}(t) \rangle = \text{Re}[\mathbf{p}^* \cdot \nabla \bar{\mathbf{E}}^*] \quad (3.3)$$

where $\bar{\mathbf{E}}^*$ is the complex conjugation of the electric field vector. In order to use Eq. (3.3) to calculate the dielectrophoretic force on a particle it is necessary to determine the effective induced dipole moment that is formed in the particle due to the presence of an external electric field. In order to solve for the induced dipole moment in a spherical particle we will assume that the particle is placed in a uniform electric field. This assumption is valid in situations where changes in the magnitude of the electric field occur gradually and over distances much greater than the dimensions of the particle. While this assumption will not always hold true in physical situations, the analytical expressions derived here prove to be a reasonable predictor of dielectrophoretic behavior.

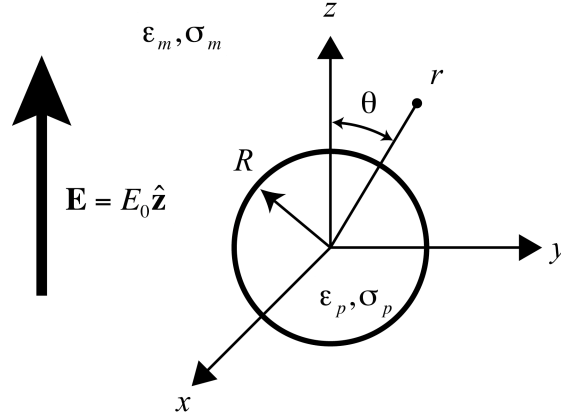


Figure 3.2

Electrically neutral particle of radius R , permittivity ϵ_p and conductivity σ_p suspended in a medium of permittivity ϵ_m and conductivity σ_m in a uniform electric field of magnitude E_0 . [Ref. 37]

Consider the spherical particle, shown in Figure 3.2, placed in a uniform electric field oriented along the z direction given by $\mathbf{E} = E_0 \hat{\mathbf{z}}$. The electric field induced inside the particle is assumed to be uniform. The electric potential outside of the particle is assumed to be a superposition of the potential associated with the uniform external electric field as well as the potential associated with the induced dipole of the spherical particle. Thus the general forms for the electric potential solutions outside and inside the particle are given by

$$\Phi_m(r, \theta) = -E_0 r \cos(\theta) + A^* \frac{\cos(\theta)}{r^2}, \quad r > R \quad (3.4)$$

$$\Phi_p(r, \theta) = -B^* r \cos(\theta), \quad r < R \quad (3.5)$$

respectively. In order to solve for A^* and B^* boundary conditions must be considered at the particle-medium interface ($r = R$). The following expressions are obtained by

imposing boundary conditions that potential must be equal and charge must be conserved at the interface.

$$\Phi_m(r = R, \theta) = \Phi_p(r = R, \theta), \quad (3.6)$$

$$\varepsilon_m^* E_m^*(r = R, \theta) = \varepsilon_p^* E_p^*(r = R, \theta), \quad (3.7)$$

where ε^* is the complex permittivity given by

$$\varepsilon^* = \varepsilon - j \frac{\sigma}{\omega}, \quad (3.8)$$

and σ and ε are the conductivity and permittivity of the material in question and ω represents the signal frequency. The solutions for A^* and B^* are then

$$A^* = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} R^3 E_0, \quad (3.9)$$

$$B^* = \frac{3\varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} E_0. \quad (3.10)$$

The electric potential associated with the induced dipole of the particle can now be written as

$$\Phi_{induced}(r, \theta) = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} R^3 E_0 \frac{\cos(\theta)}{r^2}. \quad (3.11)$$

By comparing this expression to the expression for an electric potential of a point dipole in a medium, which is given by

$$\Phi_{dipole}(r, \theta) = \frac{p_{eff}}{4\pi\varepsilon_m} \frac{\cos(\theta)}{r^2}, \quad (3.12)$$

it is clear that the effective induced dipole moment for a spherical particle is

$$\mathbf{p}_{eff} = 4\pi\varepsilon_m f_{CM(sphere)} \mathbf{E}_0, \quad (3.13)$$

where $f_{CM(sphere)}$ is given by

$$f_{CM(sphere)} = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*}. \quad (3.14)$$

$f_{CM(sphere)}$ represents the Clausius-Mossotti factor for a sphere. The Clausius-Mossotti factor can be thought of as a measure of the strength of the dipole that can be induced in a particle through the presence of an external field. A more general form of the Clausius-Mossotti for ellipsoids is given by

$$f_{CM(ellipsoid)} = \frac{\epsilon_p^* - \epsilon_m^*}{3[\epsilon_m^* + (\epsilon_p^* - \epsilon_m^*)L]}, \quad (3.15)$$

where L is the depolarization factor along an axis of the ellipsoid. For a sphere the depolarization factor is 1/3 for all axes, allowing Eq. (3.15) to simplify to Eq (3.14). For a highly anisotropic prolate spheroid, where one axis is much longer than the other two, the depolarization factor is 0 along the long axis and 1/2 along the two short axes. The highly anisotropic prolate spheroid is found to be a reasonable approximation to a cylindrical nanowire.³⁹

By combining Eq. (3.3) and Eq (3.13) it is possible to arrive at the following expression for the translational dielectrophoretic force,

$$F_{DEP} = c \epsilon_m \text{Re}[f_{CM}] \nabla E_{RMS}^2 \quad (3.16)$$

where c represents a pre-factor containing information about the geometry of the particle. Thus, to utilize and optimize dielectrophoresis to position and place a specific nanowire, the variables we have to work with are the medium in which the nanowire is suspended, specifically its permittivity and conductivity, the geometry of the

electrodes used to generate the electric field, which will determine the field gradients acting on the nanowire, and the magnitude and frequency of the electric field, which will influence the strength and the polarity of the induced dipole in the nanowire and the magnitude of the force.

3.1.2 DEP and nanowires

Dielectrophoresis has already been shown to be an effective tool in manipulating 1-dimensional semiconductor structures. As early as 1998, Yamamoto et al. reported the use of an AC electric field to manipulate and orient carbon nanotubes.⁴⁰ In their experiment a drop of isopropyl alcohol containing carbon nanotubes was placed over two parallel planar electrodes separated by 400 μm . By driving the electrodes at frequencies ranging from 10 Hz to 10 MHz they were able to collect carbon nanotubes at the edge of both electrodes oriented perpendicular to the electrode edge as shown in Figure 3.3. The nanotubes were manipulated through dielectrophoresis whereby nanowires were attracted to areas of high field gradient (the edge of the electrodes) and oriented with their axis along the electric field (perpendicular to the electrode edge).

In 2000 Smith et al. successfully used dielectrophoresis to align and position Au nanowires to bridge a gap between two electrodes such that each end of the nanowire was in physical contact with an electrode.³⁵ In doing so they demonstrated that it is possible to orient and place individual nanowires at specified locations in a deterministic way using dielectrophoresis. In their work, Au nanowires suspended in

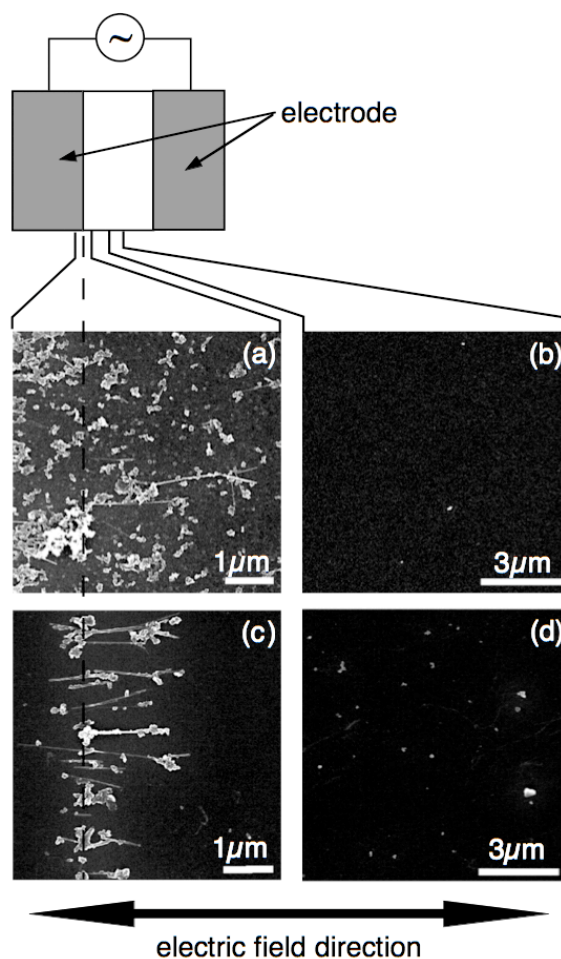


Figure 3.3

SEM images [of DEP aligned carbon nanotubes] prepared at an electric field of $2.2 \times 10^3 \text{ V}_{\text{rms}} \text{ cm}^{-1}$ with frequency of 10 Hz for (a) and (b), and 10 MHz (c) and (d); (a) and (c) were taken at the electrode's edge and (b) and (d) in the middle of gap between two electrodes [Ref 40].

isopropyl alcohol were successfully placed across the electrodes using signal frequencies of 1 kHz. The electrodes were specifically designed to encourage nanowires to be aligned at specific locations. Because the wires were positioned at a known location it was possible to fabricate contacts and probe pads in order to electrically characterize the Au nanowires.

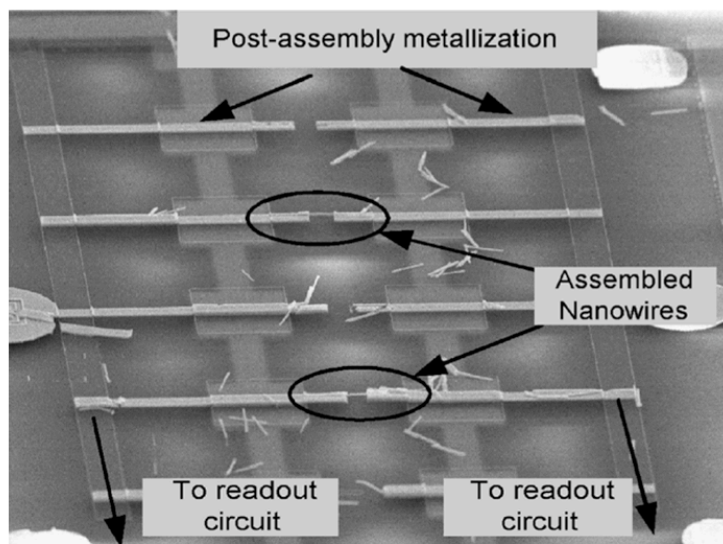


Figure 3.4

SEM photograph of assembly sites initially electrically isolated from the readout circuitry. [DEP] Assembled nanowires are clamped and connected to the readout circuit using a post-assembly e-beam lithography and metallization step [Ref. 59].

In the past few years significant work has been done to demonstrate the effectiveness of dielectrophoresis on a variety of 1-dimensional structures including carbon nanotubes,⁴⁰⁻⁴⁴ metallic nanowires (Au ^{35,45,46} and Ag ,^{46,47}) oxide nanowires (Ga_2O_3 ,⁴⁷ SnO_2 ⁴⁷⁻⁴⁹ and ZnO ,⁵⁰⁻⁵²) and semiconductor nanowires (GaN ,^{47,-55} InP ⁵⁶ and Si ⁵⁷).

Much of the work cited thus far has used dielectrophoresis as a means to study and characterize individual nanowires. Efforts have also been made to utilize dielectrophoresis as a means to integrate nanowires into larger functional systems. In 2004, Evoy et al. proposed the use of dielectrophoresis to position and integrate nanowires with mixed-mode CMOS circuitry.⁵⁸ In 2006 the actual integration with CMOS based electrodes was performed and studied by Narayanan, et al.⁵⁹ In their

work they were able to demonstrate the integration of metal nanowires with CMOS based electrodes as shown in Figure 3.4. While they were able to demonstrate that it may be possible to use dielectrophoresis to integrate nanowires with a larger system their example image shows very few alignment sites which actually achieved successful nanowire alignment. Furthermore there are many stray nanowires that have been deposited on the circuit at undesired locations. Such stray wires could ultimately be a significant problem in more complicated systems and must be addressed. In order to use dielectrophoresis as an effective tool for constructing large systems it is necessary to understand the parameters that govern dielectrophoresis and how to optimize them to place wires at specified locations and only those locations.

In 2006 Lee et al. performed a systematic study to determine optimal dielectrophoretic parameters for GaN nanowires.⁶⁰ Specifically, they examined the effects of signal amplitude and frequency. In their experiment they placed a drop of nanowire suspension over 200 alignment sites which were driven at signal amplitudes of either 10 or 15 V_{pp} and signal frequencies of 10 kHz or 20 MHz. Figure 3.5 shows plots of the percentage of alignment sites that resulted in an aligned nanowire under various signal conditions. From their results they concluded that lower signal frequency and greater signal amplitude result in a greater percentage of successful alignment sites. Their alignment sites are rather large (several microns in width), limiting the precision necessary to achieve successful alignment. While the experiment clearly conclude that stronger DEP force is achieved at lower frequencies it does not examine specific parameters necessary to use DEP to place nanowires with

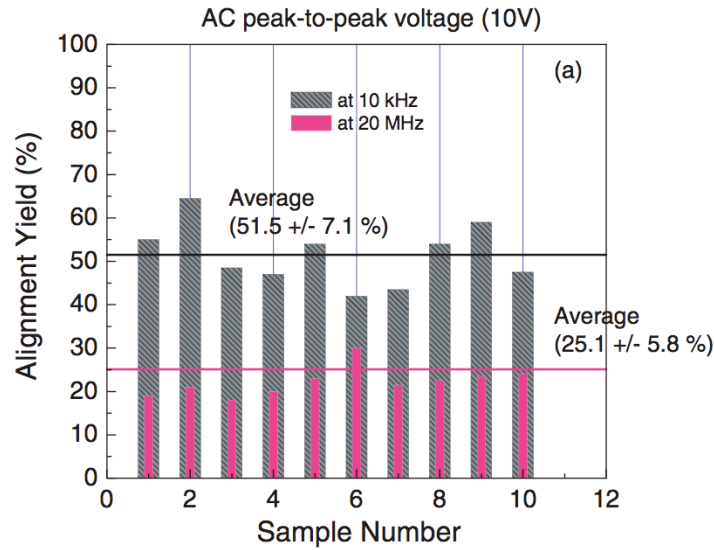


Figure 3.5

The distribution of the yield rate for aligned GaN nanowires in the gap over the 200 electrode array with 10 V_{pp} at the frequencies of 10 kHz and 20 MHz [Ref. 60]

great precision. Furthermore, this study primarily focuses on aligned wires and does not quantify stray nanowires which have been placed in undesired locations. Optimizing dielectrophoretic parameters to minimize such wires will be important in order to utilize dielectrophoresis in the assembly of practical nanowire systems.

In this chapter we will examine the use of dielectrophoresis to manipulate and place InAs nanowires. In section 3.2 experiments using low signal frequency and large electrodes will be used in order to determine the feasibility of using dielectrophoresis to manipulate InAs nanowires. In section 3.3 dielectrophoresis will be studied as a means to place nanowires with great precision at desired locations, and only those locations. Section 3.4 will present a detailed analysis of the various parameters that were optimized in section 3.3 and the role they play in using dielectrophoresis as a means to precisely place nanowires.

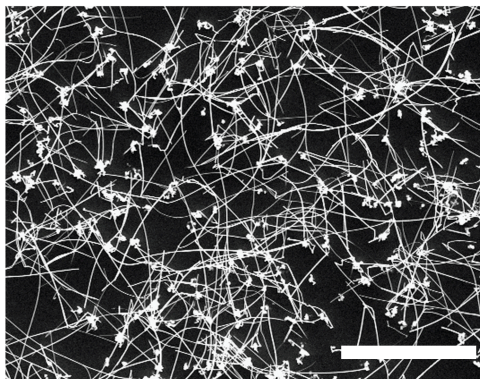


Figure 3.6

SEM image of as grown InAs nanowires on an SiO_2 substrate. The wires are approximately 60 nm in diameter and 20 μm in length before sonication. Scale bar is 10 μm .

3.2 Low Frequency DEP Manipulation

In order to determine the feasibility of using DEP as a means to manipulate InAs nanowires, preliminary experiments were carried out using fairly large electrodes. These experiments were performed to understand the influence DEP exhibits on InAs nanowires and were not necessarily concerned with the precision with which they are finally aligned. These experiments yielded significant insights into the relationship of the medium in which the nanowires are suspended and signal conditions.

3.2.1 Experimental Setup and Procedure

InAs nanowires were grown by metal-organic chemical vapor deposition. 40 nm Au particles were dispersed across the surface of a 600 nm layer of thermally grown SiO_2 , in order to act as catalysts and nucleation points for nanowire growth.

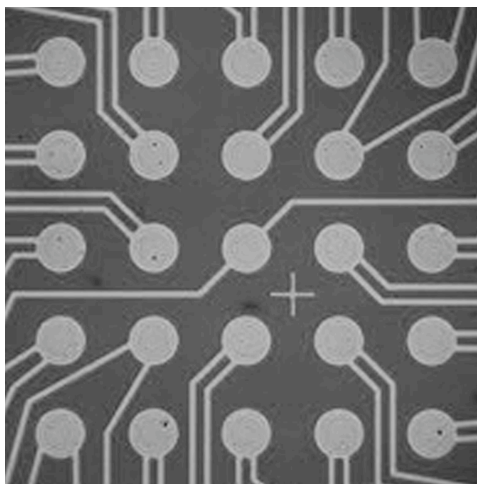


Figure 3.7

Commercially fabricated 5 x 5 electrode array with 100 μm diameter electrodes.

The growth was carried out for 10 minutes in a horizontal chamber at 350° C under 100 Torr chamber pressure using trimethylindium and arsine in H_2 carrier gas at an input V/III ratio of ~ 50 . The resulting nanowires have diameters of ~ 60 nm and lengths of ~ 20 μm and are shown in Figure 3.6. The nanowires were then suspended into de-ionized water (DI water, resistivity = 18.2 $\text{M}\Omega\text{-cm}$) or isopropyl alcohol (IPA). After suspension, the nanowire lengths were between 5 μm and 20 μm .

An optical image of the electrodes used in this experiment is shown in Figure 3.7. The electrode array was commercially fabricated by Nanogen and consisted of Pt electrodes on a SiO_2 covered Si substrate. A passivation layer of SiO_2 covers the leads out to the pads such that only the circular electrodes are exposed. The electrodes are arranged in a 5 x 5 array. Each circular electrode is 100 μm in diameter and the electrodes are spaced 100 μm apart from one and other.

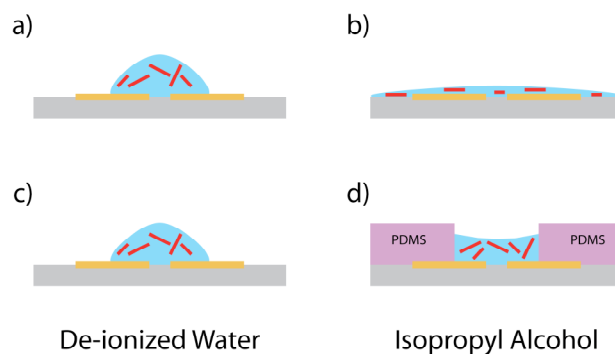


Figure 3.8

Schematic diagram showing how de-ionized water solutions (a,c) and isopropyl alcohol solutions (b) wet the surface of the DEP chip. Because of the differing contact angles the distribution of nanowires above the electrode will be very different in the two cases. In order to perform a direct comparison a PDMS “cup” is used to contain the isopropyl alcohol (d) to allow for a better comparison to di-ionized water solutions (c).

For each experiment, a micropipette was used to place 3 μL of nanowire solution over the entire DEP electrode array. Two adjacent DEP pads were then driven using a sinusoidal signal with a peak-to-peak voltage of 150 Volts at frequencies of either 2 kHz or 20 kHz. After several minutes the drops were removed and the signal was turned off. The DEP chips were then inspected using optical and scanning electron microscopy. An HP33120A function generator was used to generate a sinusoidal AC signal, which was then amplified using an audio signal amplifier (TOA P-924MK-2).

In applying the nanowire solutions to the DEP chip, the DI-water based solutions exhibited a fairly large contact angle resulting in a well formed drop on the surface of the chip, as illustrated in Figure 3.8 (a) and (c), whereas the IPA based solution resulted in a low contact angle, wetting the entire surface of the DEP chip as shown in Figure 3.8 (b). This difference in droplet shape has a considerable effect on

the spatial distribution of nanowires relative to the DEP electrodes as illustrated in Figure 3.8 (a) and (b). As a result, polydimethylsiloxane (PDMS) “cups” were fabricated and adhered to the surface of the DEP chips for use in the IPA solution experiments, as shown in Figure 3.8 (d), to allow for a more valid comparison between the performance of the two mediums. A detailed discussion on the fabrication of these cups can be found in Appendix A.

3.2.2 Experimental Results

The electric field lines that form between two circular electrodes will radiate outward, perpendicular to the edge of the electrode. The magnitude of the gradient of the electric field will be greatest immediately around the perimeter of the electrodes and will drop off with distance. Thus if DEP is the dominant force in positioning nanowires, the translational component of DEP is expected to collect nanowires around the perimeter of the circular electrode while the torque component of DEP is expected to align the nanowires such that they point outward in a radial fashion, perpendicular to the edge of the circular electrode.

Figure 3.9 shows SEM images of the DEP electrodes after nanowire placement. Images are shown for electrodes that were driven at 2 and 20 kHz for solutions using both IPA and DI water as their medium. By inspection it is clear that in all cases nanowires have been collected around the perimeter of the electrodes suggesting that DEP was able to influence the InAs nanowires in both IPA and DI water. Upon closer inspection, Figure 3.9 (a) and (b) suggest that increasing

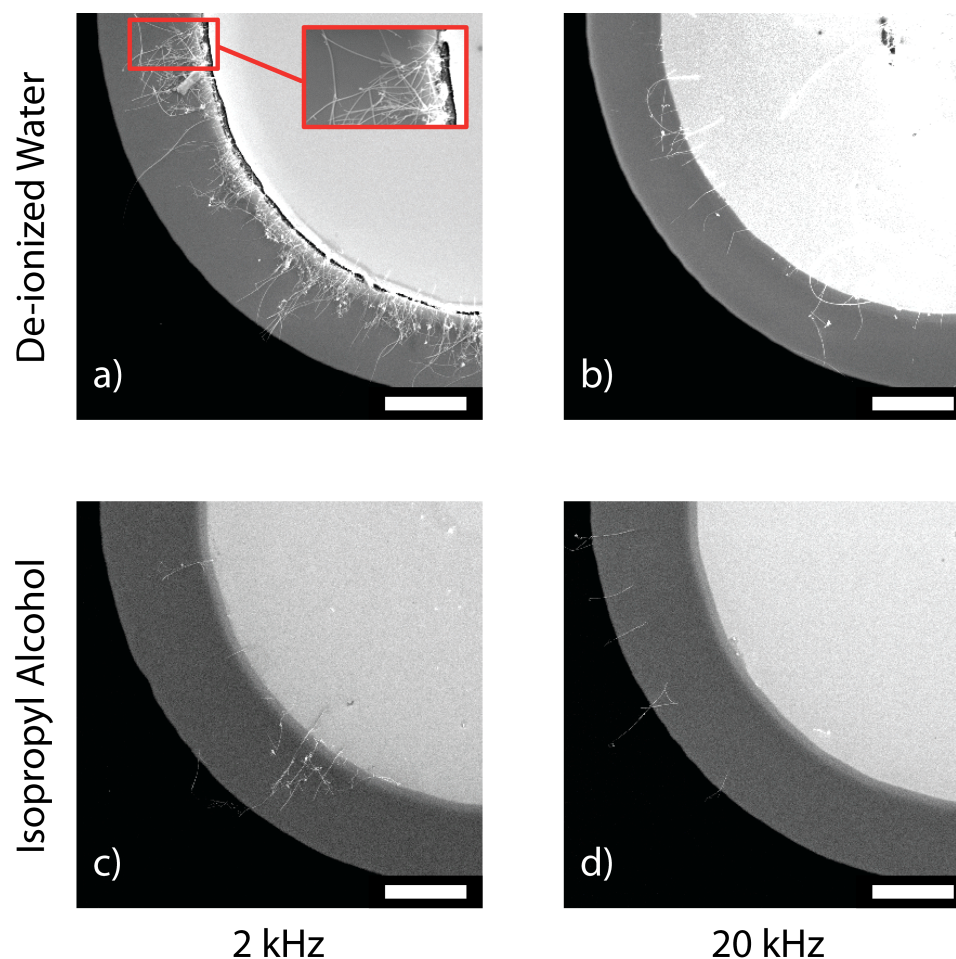


Figure 3.9

SEM images of DEP electrodes after nanowire placement. Images are shown for nanowires suspended in de-ionized water and positioned using signal frequencies of 2 kHz (a) and 20 kHz (b) and nanowires suspended in isopropyl alcohol and positioned using signal frequencies of 2 kHz (c) and 20 kHz(d).

frequency for nanowires suspended in water seems to reduce the total number of wires collected, but tends to align those wires in a somewhat more radial fashion along the electric field. Figures 3.9 (c) and (d) show that in both cases relatively few wires were collected, but those that were followed a strong radial arrangement. Figure 3.9 (a) also shows that low frequency conditions in DI water result in electrode damage not observed in the other three cases.

3.2.3 Analysis

Given that InAs nanowires are much more conductive than either medium (IPA or DI water) the DEP force is expected to be positive (meaning wires are attracted to areas of high electric field gradient) and decrease with increasing signal frequency. Because the DEP force decreases we would expect a reduction in translational force on the nanowires, which should result in fewer nanowires collected at the electrode edge, as well as a reduced torque force on the nanowires, which should result in a less precise radial alignment. Figures 3.9 (a) and (b) show, that for nanowires suspended in water, increasing frequency results in fewer wires, but with increased alignment. This suggests that at low frequencies the dominant force may not be DEP and other mechanisms must be considered. Figures 3.9 (c) and (d) show that for nanowires suspended in IPA, frequency seems to have little effect on alignment, but that the magnitude of the DEP force does seem to slightly decrease with increasing frequency.

3.2.3.1 Electro-osmotic Fluid Flow

In describing DEP we have focused on the electric field's influence on a particle suspended in solution. It is also important, however, to consider the influence exerted on the solution itself.³⁸ When a potential is applied across two electrodes separated by a fluidic medium the charges in the medium (such as ions or contaminants) will redistribute according to the polarity of the electrodes. This results

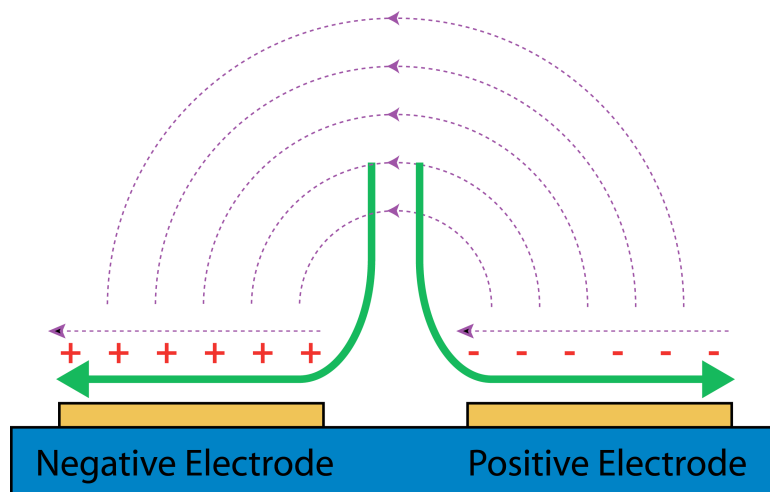


Figure 3.10

Schematic illustration of electro-osmotic fluid motion. A charge layer of ions builds up at the fluid-electrode interface (shown in red). The electric field along the electrode (shown in purple) results in an electrostatic force which drags the charged layer along the surface of the electrode causing a fluidic motion, shown in green.

in a layer of “charged solution” at the interface between the solution and electrode. Because the electric field between the two electrodes has a tangential component that runs parallel to the surface of the electrode, the charged layer will be driven along the surface of electrode by electro-static force. As the charges move they will drag the fluid along as well resulting in a fluidic motion known as *electro-osmotic motion*.^{38,61} Because the formation of this charge layer at the electrode interface is heavily dependent on signal amplitude, signal frequency, and conductivity of the medium, all of these variables are expected to play a large role in the strength of the electro-osmotic motion effect. Electro-osmotic motion is illustrated schematically in Figure 3.10.

In 2000 Green et al. characterized this effect extensively by measuring the electro-osmotic velocity under various signal conditions.⁶¹ In their study they

demonstrate that increasing the signal frequency reduces electro-osmotic motion. This is because as signal frequency is increased the charges in solution have less time to respond and form the charged layer at the electrode-solution interface. They also demonstrate that the influence of electro-osmotic motion is greatly reduced as the conductivity of the medium is decreased.

Thus for the low frequency signal conditions with nanowires suspended in DI water, depicted in Figure 3.9 (a), electro-osmotic motion is expected to play a significant role. Monitoring the experiments using an optical microscope reveals that there does appear to be more violent fluidic motion at lower frequencies. We believe that this motion results in a “stirring” of the solution which disturbs the radial alignment of nanowires collected through DEP. We also believe that this fluidic motion plays a role in the dramatic increase in the number of wires collected at low frequencies (shown in Figure 3.9 (a)) which would not be expected through DEP alone. Fluidic motion increases the number of wires collected by drawing distant nanowires closer to the electrode where they will fall under the influence of DEP force. As the frequency is increased (as shown in figure 3.9 (b)) the electro-osmotic motion becomes less significant and nanowires are able to achieve a more radial alignment as would be predicted by DEP theory. Figure 3.9 (c) and (d) show that an increase in frequency has no effect on radial alignment and does seem to result in slight decrease in the magnitude of DEP. Because the conductivity of IPA is less than that of DI water, electro-osmotic motion does not play a significant effect and thus DEP is expected to be the dominant force.

3.2.4 Experimental Conclusions

From these experiments it is clear that working at higher signal frequencies will allow for DEP to be the dominant mechanism in positioning and placing nanowires. These studies also suggest that working at higher frequencies also protects the electrodes from damage, which likely occurs due to local pH changes and electrochemical effects in water. While these experiments suggest that IPA based solutions will be more resistant to electro-osmotic effects, they also demonstrate that DI water at high frequency can be used to effectively align nanowires.

3.3 Precision DEP Alignment

In this section we demonstrate the ability to place InAs nanowires with great precision using DEP. The experimental setup and observations are presented in this section. An in depth analysis of the relevant parameters and their effects are presented in Section 3.4

3.3.1 Experimental Setup and Procedure

InAs nanowires were grown by metal-organic chemical vapor deposition. 40 nm Au particles were dispersed across the surface of an n-InAs (111)B substrate in order to act as catalysts and nucleation points for nanowire growth. The growth was

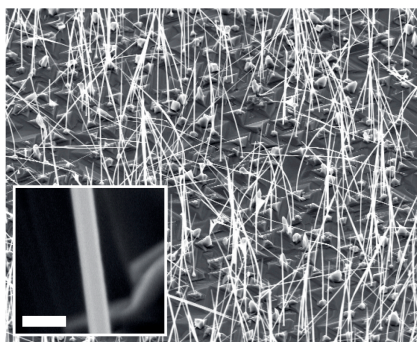


Figure 3.11

SEM image of as grown InAs nanowires before suspension. Scale bar is 10 μm for figure, 200 nm for inset.

carried out for 40 minutes in a horizontal chamber at 500° C under 100 Torr chamber pressure using trimethylindium and arsine in H_2 carrier gas at an input V/III ratio of 64. The resulting nanowires have diameters of ~ 150 nm and lengths of ~ 20 μm and are shown in Figure 3.11. The nanowires were then suspended into 150 μL of de-ionized water (resistivity = 18.2 $\text{M}\Omega\text{-cm}$). After suspension, the nanowire lengths were between 12 μm and 20 μm and the solution is believed to have had a density of ~ 1000 -2000 wires/ μL .

Electrodes were constructed using standard micro-fabrication techniques in order to serve as a framework on which to align the suspended nanowires. An insulating substrate was first prepared using PECVD to deposit 500 nm of SiN_x on Si. Metal alignment electrode arrays comprised of 10 nm Ti and 90 nm Au were then patterned using e-beam lithography and e-beam evaporation followed by a standard lift-off procedure. The electrode arrays were made up of a set of alignment sites, each of which has two 1 μm wide fingers with a 10 μm gap between them, as shown in

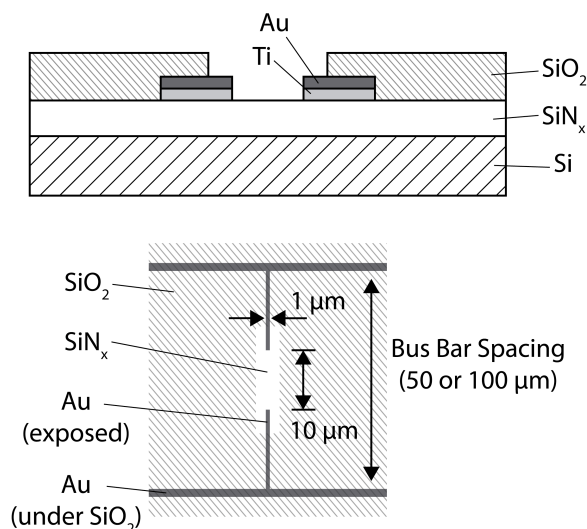


Figure 3.12

Schematic diagram of electrode layer structure (top) and top-view of alignment site (bottom).

Figure 3.12. PECVD was then used to deposit 250 nm SiO₂ over the entire metal structure. E-beam lithography followed by a wet etch in buffered oxide etch (BOE) was then carried out to remove the oxide layer at each alignment site. Electrode arrays were fabricated in groups of 50 alignment sites with 100 μm spacing between bus bars, or 100 alignment sites with 50 μm spacing between bus bars. Figure 3.12 shows a schematic of the electrode layer structure and relevant dimensions for an alignment site. A detailed description of the fabrication of these electrode arrays can be found in Appendix B.

Six sets of DEP electrode arrays (DEP chips) are considered in the experiment. 3 of them contain 100 alignment sites with 50 μm bus bar spacing while the other 3 contain 50 alignment sites with 100 μm bus bar spacings. In each of the six experiments a micropipette was used to apply 2 μL of nanowire solution to the surface

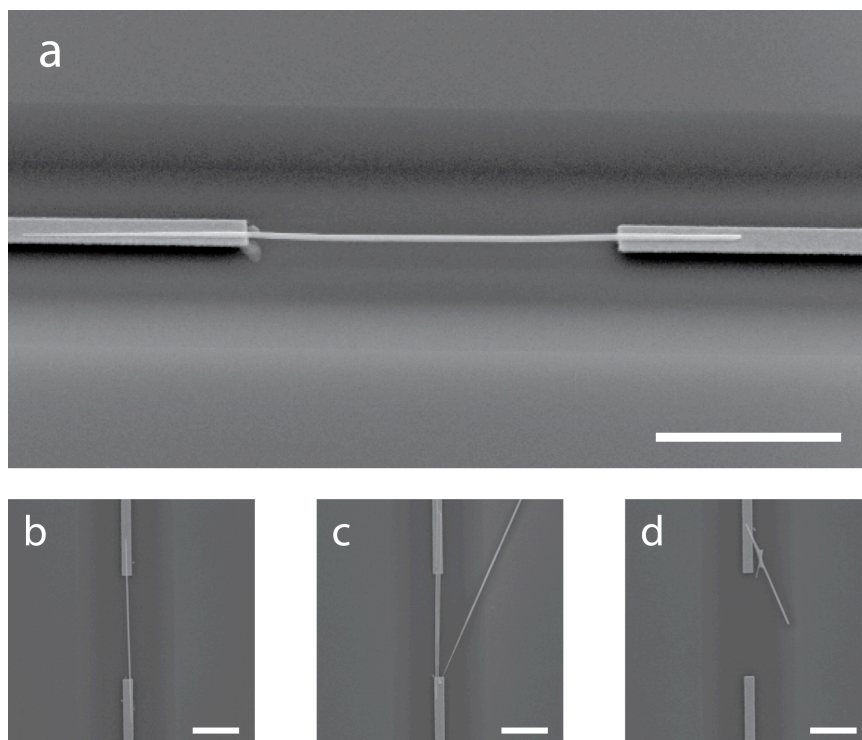


Figure 3.13

SEM images of individual alignment sites after DEP alignment. SEM image of a precisely aligned nanowire taken at 45° (a), and from directly overhead (b). SEM image of an alignment site with both precise alignment and a stray nanowire (c). SEM image of an alignment site with just a stray wire (d). Scale bar is 5 μm for all images.

of the DEP chip completely covering all available alignment sites. An HP33120A function generator was used to apply a sinusoidal signal across the alignment sites with a peak-to-peak voltage of 10 Volts and signal frequencies of either 10 kHz, 1 MHz or 10 MHz. After precisely 3 minutes dry nitrogen was used to blow the 2 μL drop of solution off of the chip. Once the drop was removed, the AC signal was turned off and the chips were examined using optical and scanning electron microscopes.

3.3.2 Experimental Results

Inspection revealed that the vast majority of wires left behind after drop removal were in physical contact with a metal electrode at an alignment site. Wires that were not in contact with an electrode were swept away when the drop was blown off. The wires that were in contact either bridged the alignment site gap as shown in Figures 3.13 (a), 3.13 (b) and 3.13 (c) or only had contact with one of the two alignment fingers as shown in Figures 3.13 (c) and 3.13 (d). Figure 3.13 (c) indicates that it is possible to have both bridging and non-bridging events at the same alignment site. Wires that bridge the gap at alignment sites (as shown in 3.13 (a), 3.13 (b) and 3.13 (c)) will be referred to as precisely aligned wires. Wires that are only in contact with one finger at an alignment site (as shown in figures 3.13 (c) and 3.13 (d)) will be referred to as stray wires.

3.3.2.1 Post Alignment Electrical Contact

Wires that were successfully aligned (as shown in Figures 3.13 (a), 3.13 (b) and 3.13 (c)) did not immediately make electrical contact with alignment electrodes. This is likely due to a thin layer of oxide that is believed to form on the surface of the InAs nanowire after removal from the growth chamber. To verify this, 3 alignment sites with a total of 4 aligned wires between them were chosen at random. Further micro-fabrication was carried out on the already aligned wires to pattern metal contacts over the tips of the aligned nanowires. E-beam lithography was used to define the contact areas. A 30 second wet oxide etch (in BOE) immediately followed

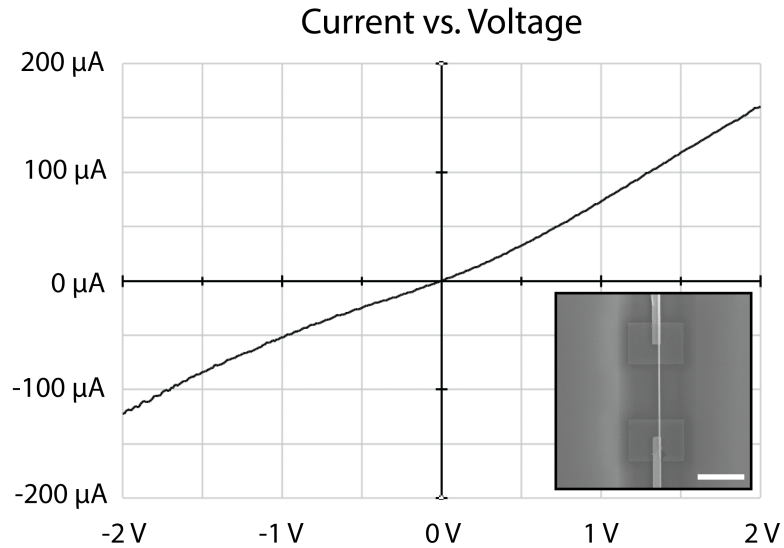


Figure 3.14

IV curve of 4 aligned nanowires in parallel. Inset shows an SEM image of one such aligned wire after micro-fabrication has been carried out to remove oxide and deposit metal to make contact electrical contact with the alignment site. Scale bar for the inset is 5 μm .

by e-beam evaporation and lift-off was used to pattern metal contacts (15 nm Ti / 90 nm Al) over the nanowire and electrode tips. A fabricated contact and measured IV curve are shown in Figure 3.14. The resistance of each nanowire is found to be approximately 60 k Ω and demonstrates that the InAs nanowires maintain their electrical properties through the alignment process and are similar to those reported in the literature.⁶² In order to make ohmic contact to InAs nanowires, a BOE dip is typically required.^{6,8}

3.3.2.2 Large Scale Nanowire Alignment

Figure 3.15 shows optical microscope images of each DEP chip after the alignment experiment. The left column shows three chips with 100 alignment sites

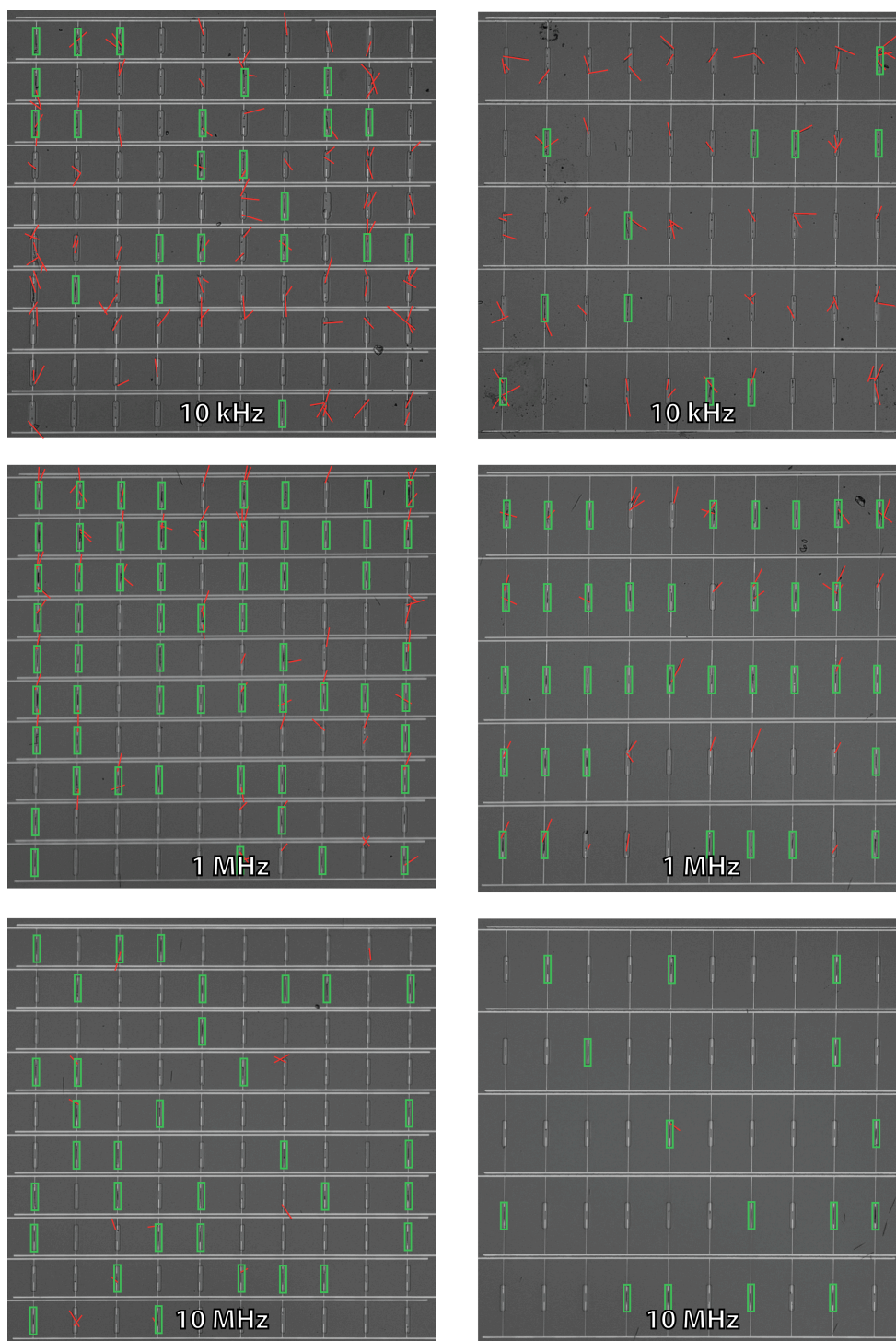


Figure 3.15

Optical microscope images of electrode arrays after DEP alignment. Precisely aligned sites are highlighted with a green box, stray wires are highlighted with red line. Each image is 500 x 500 μm .

Percentage of Aligned Sites

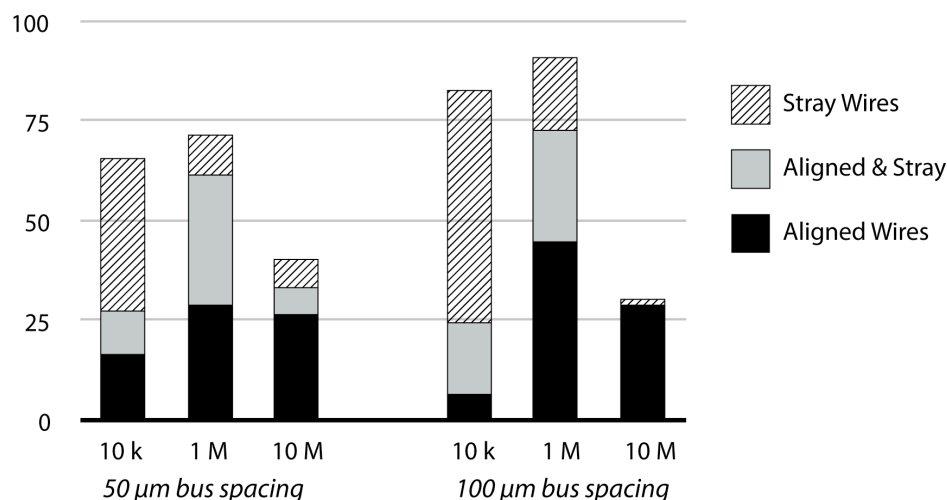


Figure 3.16

Histogram showing the percentage of alignment sites which attracted nanowires. Each bar is broken up to show the percentage of alignment sites which had only precisely aligned wires, both aligned and stray wires, and only stray wires. The histogram shows that with increasing frequency there is a decrease in the total number of wires collected but an increase in the precision with which wires are collected.

(and 50 μm bus bar spacing) that were driven at 10 kHz, 1 MHz, and 10 MHz respectively. The right column contains images of three chips with 50 alignment sites (and 100 μm bus bar spacing) that were also driven at 10 kHz, 1 MHz, and 10 MHz respectively. Perfectly aligned sites are highlighted with a green box and stray wires are highlighted with red lines to make them easier to see. The average number of nanowires collected per site is approximately 1.5 at lower frequencies and drops to 0.5 at higher frequencies. Of the wires collected only about 50% of them are precisely aligned at lower frequencies where as 80% of them are precisely aligned at higher frequencies. Figure 3.16 plots the percentage of alignment sites that had only perfectly aligned wires, both aligned wires and stray wires and only stray wires. From

Figure 3.16, around 75% of alignment sites attracted nanowires at lower frequencies compared to 30% at higher frequencies, but the fraction of those sites that achieved precision alignment is much greater at higher frequencies. From Figure 3.15 and 3.16 it is clear that by increasing signal frequency the total number of collected wires decreases. However, at higher frequencies a greater percentage of those collected wires are precisely aligned with few stray wires.

3.4 Precession DEP Analysis

In section 3.3, experiments were presented in which InAs nanowires are positioned with great precision using DEP. In this section observations from section 3.3 are examined in order to determine important parameters in DEP alignment and how they can be utilized to align wires in a deterministic fashion.

3.4.1 Effect of Signal Frequency

The frequency dependence of the total number of wires collected, as well as the precision with which they are collected, can both be explained by understanding the variables that effect DEP force. For a nanowire, the external electric field-induced dipole inside the nanowire will result in a torque force, which will cause the nanowire to align with its long axis along the electric field, as well as a translational force that is a function of the electric field gradient. As discussed in section 3.1, the translational

dielectrophoretic force on a spheroid is governed by the well-known analytical expression,³⁶⁻³⁸

$$F_{DEP} = c \epsilon_m \text{Re}[f_{CM}] \nabla E^2 \quad (3.16)$$

where c represents a pre-factor containing information about the volume of the nanowire, ϵ_m represents the permittivity of the medium, f_{CM} is the Clausius-Mossotti factor and contains information about the permittivities of both the medium (in this case de-ionized water) and the InAs nanowire as well as the signal frequency, and finally E which represents the magnitude of the electric field. While the above expression is given for a spheroid it has been shown that a prolate spheroid serves as a reasonable approximation for a cylindrical particle with a high aspect ratio³⁹ and thus allows the use of analytical expressions to examine the DEP force on nanowires.

The dielectrophoretic force equation suggests that the frequency dependence of the translational motion of a nanowire is embedded in the Clausius-Mossotti factor. The Clausius-Mossotti factor is a measure of the strength of a dipole that can be induced in a particle through the presence of an external field. For a nanowire, the Clausius-Mossotti factor is anisotropic and thus, the resulting DEP force will depend on the orientation of the electric field gradient with respect to the orientation of the nanowire, which in turn is determined by the direction of the electric field. In situations where the field gradient is oriented parallel to the electric field only the Clausius-Mossotti factor along the long axis of the nanowire must be considered to calculate the direction and magnitude of the translational force and this factor is given by^{37,38}

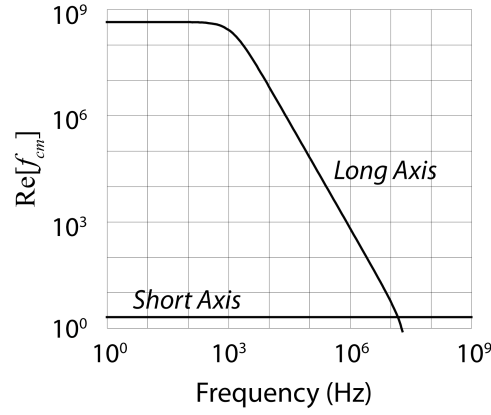


Figure 3.17

Plot of the real part of the Clausius-Mossotti for the long and short axes of an InAs nanowire suspended in de-ionized water as a function of signal frequency.

$$f_{CM(long\ axis)} = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*}. \quad (3.17)$$

In situations where the gradient of the electric field is perpendicular to the electric field (and thus also perpendicular to the long axis of the nanowire) it is only necessary to consider the Clausius-Mossotti factor along the short axis of the nanowire, which is given by^{37,38}

$$f_{CM(short\ axis)} = 2 \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + \epsilon_m^*}. \quad (3.18)$$

In cases where the gradient is neither parallel nor perpendicular to the nanowire it is necessary to consider the effect of both the short axis and long axis Clausius-Mossotti factor in order to determine the magnitude and direction of the DEP force. Calculating and plotting the real part of the Clausius-Mossotti factor for an InAs nanowire suspended in de-ionized water (shown in Figure 3.17) reveals that at low frequencies the value along the long axis of the wire is several orders of magnitude larger than the

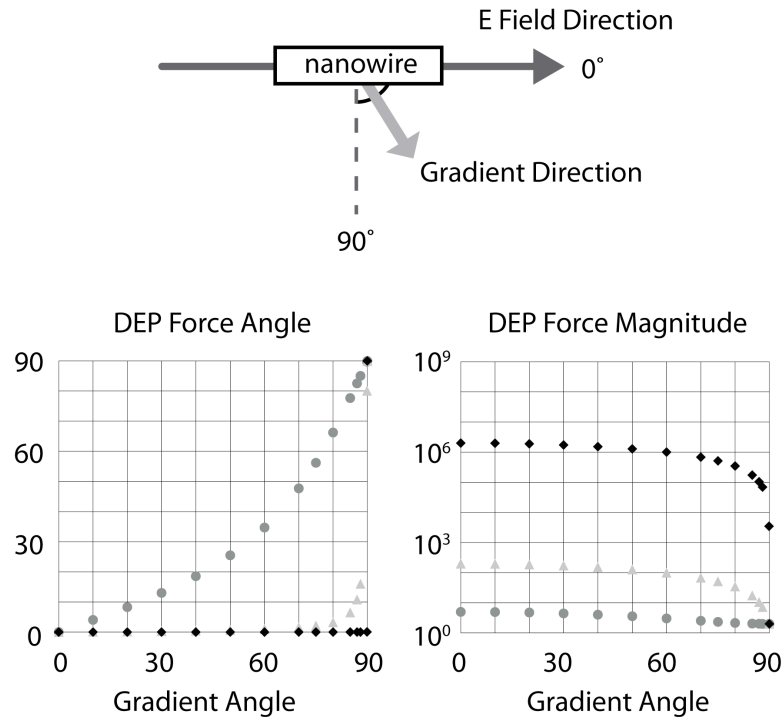


Figure 3.18

Diagram of a nanowire in an electric field pointing to the right with an arbitrary electric field gradient (top). DEP force angle and relative force magnitude are plotted as a function of gradient direction angle for signal frequencies of 10 kHz (diamonds), 1 MHz (triangles) and 10 MHz (circles).

short axis, but decreases to a value much closer to the short axis value at higher frequencies. Figure 3.18 shows plots of the calculated direction and magnitude of the resulting DEP force as a function of the electric field gradient orientation with respect to the nanowire orientation at different signal frequencies. At low frequencies the DEP force is expected to be large and dominated by the long axis Clausius-Mossotti factor. As a result nanowires will tend to move along the electric field lines at lower frequencies, whereas at higher frequencies the dominance of the long axis Clausius-Mossotti factor is reduced resulting in wires experiencing a translational force that is more along the gradient of the electric field. The large magnitude of the Clausius-

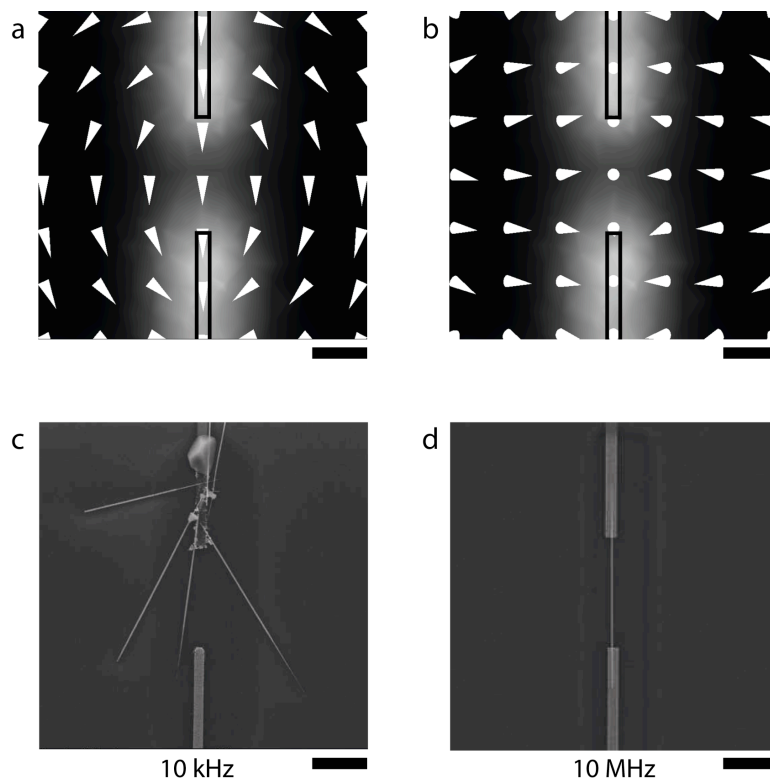


Figure 3.19

(a) and (b) both show finite element simulation results 5 μm above an alignment site. The white arrows represent the electric field direction (a) and electric field gradient direction (b). The shading of both (a) and (b) represent the magnitude of the gradient vector squared (which corresponds to DEP force) on a linear scale where lighter shading indicate a greater value. Figures (c) and (d) are SEM images of representative alignment sites at signal frequencies of 10 kHz and 10 MHz respectively. Scale bars are 5 μm for all images.

Mossotti factor at low frequencies accounts for the greater number of wires that are collected at lower frequencies.

In order to understand the impact of the Clausius-Mossotti factor on precision alignment it is necessary to consider the geometry of the electric field for the electrode structure used in this experiment. Three dimensional finite element analysis using the COMSOL software package was employed in order to calculate the electric field and field gradient near an alignment site. Detailed simulation parameters can be found in

Appendix C. Figures 3.19 (a) and (b) show the resulting calculations for electric field direction, electric field gradient and magnitude of the electric field gradient squared, immediately around an alignment site 5 μm above the alignment electrodes. Because the gradient of the electric field drops off quickly with distance from the electrode it should be noted that the DEP force acts primarily on wires which are already close to an alignment site. At low frequencies such wires will follow the electric field lines back to one of the two electrodes at an alignment site, whereas at higher frequencies such wires will follow the gradient and be more likely to contact both electrodes at an alignment site. Thus at lower frequencies we would expect to find more wires that are only touching one of the two electrodes at an alignment site, whereas at higher frequencies we would expect to observe a greater percentage of wires bridging the gap. In looking at the SEM images in Figures 3.19 (c) and (d) and the optical images in Figure 3.15 it is clear that this is the case, and that at higher frequencies most of the collected wires are precisely aligned, whereas at lower frequencies a large fraction of the collected wires are only in contact with one of the electrodes at an alignment site.

3.4.2 Macroscopic Electrode Design

Because the electric field gradient drops off quickly with distance from the electrode, in order to achieve precision alignment it is necessary for wires to be free to move sufficiently close to an alignment site so that they will come under its influence and be aligned. To this end, it is important to consider the macroscopic electrode structure used to organize alignment sites. In this experiment a “double bus bar”

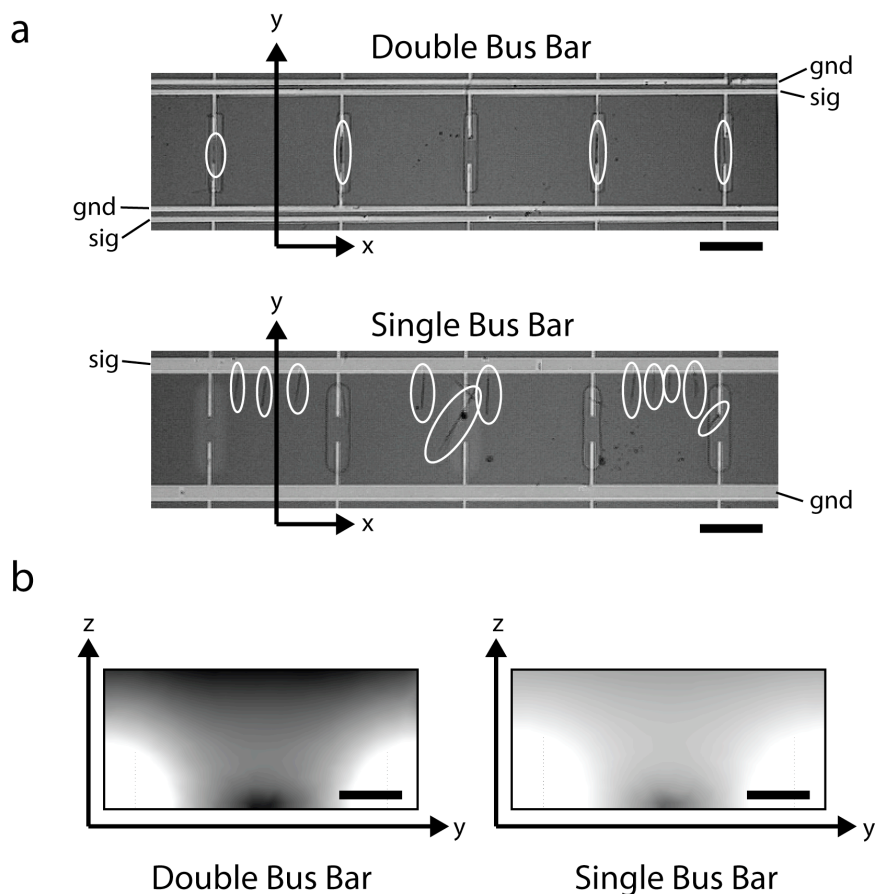


Figure 3.20

(a) shows optical microscope images of 5 alignment sites in both double and single bus bar architectures after DEP alignment. Circles indicate nanowire positions after alignment attempt. (b) shows the results of finite element simulations for the gradient of the electric field squared (which corresponds to DEP force) on a logarithmic scale where lighter shading indicate a greater value. The simulation is for a cross-sectional plane directly between two alignment sites as indicated by the location of the axis in the images in (a). Scale bars are 25 μm for (a) and 10 μm for (b).

architecture was used. In this design the bus bar is comprised of both a positive signal and ground signal which are very close together (as shown in Figure 3.20 (a)). Figure 3.20 (a) shows a comparison of alignment attempts at a moderate frequency of 1 MHz for both the double bus bar and single bus bar structure (where a much greater distance separates the positive and ground signals). It is clear that precision alignment is more

likely to occur in the double bus bar structure, and that nanowires are more likely to be attracted directly to the bus bars in the single bus bar structure. This is because the electric field gradient from the double bus bar, while very great immediately around the bus bar itself, drops off more quickly with distance making the double bus bar less visible to wires that might be floating above an alignment site. The electric field gradient in the single bus bar structure drops off much more slowly with distance and is thus able to influence and attract wires that are further away and may be above the alignment site, pulling them down to the bus bar and preventing precision alignment.

The double and single bus bar the electrodes were modeled using three dimensional finite element simulations to illustrate the differing nature of the electric field and field gradients of these two electrode geometries. Details of the model can be found in Appendix C. Figure 3.20 (b) shows a cross section of the magnitude of the electric field gradient squared as a function of position in the region between two alignment sites and above the surface of the electrode array (the y-z plane). The lighter regions shown in the single bus bar case in the area directly between the bus bars suggest that wires in this region will be influenced by a mild, but relevant DEP force drawing them toward the bus bars. The DEP force in this region, while small, is expected to be about one order of magnitude greater than in the double bus bar case. Thus, in the single bus bar case, it is expected that a wire floating as close as 20 μm above an alignment site is still likely to come under the influence of the single bus bar, and move towards it, rather than to be influenced and drawn into an alignment site. This is consistent with experimental observations, which show the single bus bar

geometry does not allow for precision alignment in the way the double bus bar geometry does, but rather results in wires being collected at the bus bars. In examining the electrode arrays in Figure 3.15 (which all used the double bus bar geometry), as well as the corresponding histogram presented in Figure 3.16, it should be noted that the experiments conducted with 50 μm bus bar spacing and 100 μm bus bar spacing behaved in a similar manner. This suggests that the double bus bar did not have a significant effect on precision alignment and that the double bus bar successfully mitigated the influence of the bus bar on the individual alignment sites.

3.4.3 Discussion of Other Relevant Factors

While signal frequency and the double bus bar structure are very important to achieving precise alignment with few stray wires, there are a number of other variables that played a role in these experiments and should be discussed.

Earlier in this chapter comparisons were made between the use of DI-water and IPA as a suspension medium. The lower conductivity of IPA should result in a greater DEP force. Because of this the frequency at which the DEP force along the long axis of the nanowire rolls of is also pushed to higher frequencies. Thus in order to achieve precision alignment higher signal frequencies would be required which would further complicate the experimental setup in terms of instrumentation and also require more robust on-chip leads to insure the signal propagates all the way to the alignment sites. For this reason DI water proved to be the more suitable choice for

precision alignment, provided that signal frequencies are sufficiently high to prevent electrode damage and minimize the effects of electro-osmotic motion.

The electrode arrays used in these experiments have an oxide layer that covers the metallic bus bars and leads leading out to the alignment sights. This layer plays an important role in achieving precision alignment and reducing the number of stray wires. While the oxide layer does attenuates the electric field that extends into the nanowire solution in areas where alignment is not desired, it should be noted that because the oxide layer is very thin this effect is minimal. The double bus bar geometry does considerably more for preventing the attraction of stray wires than the oxide layer does. More importantly, the oxide layer does play a role in the removal of stray wires that have been attracted to bus bars by preventing the adhesion of stray wires thus allowing them to be swept away when the drop is removed. Finally, because the oxide layer is etched away at each alignment site there are recessed regions in which the aligned nanowires are placed. These recessed areas provide protection from fluidic turbulence that occurs during drop removal which could disturb already aligned nanowires. While this turbulence can be countered through the use of a stronger DEP signal, the use of the recess does allow the use of lower signal voltages which are less likely to damage nanowires and also minimizes stray nanowire deposition. Thus, while not essential, the oxide layer does play a role in assisting the precision alignment and reducing the number of stray nanowires observed in these experiments.

3.5 Conclusions

In this chapter we have demonstrated that DEP is a viable alternative for placing a relatively large number of nanowires with a high level of precision by paying careful attention to the signal frequency as well as the electrode architecture that is employed. While in our experiments we determined optimal signal conditions for InAs nanowires, with careful consideration similar methods can be applied to a wide variety of nanowire materials and configurations. In our experiments, better than 70% of alignment sites saw precise alignment at moderate frequencies, but with a number of stray wires dispersed throughout the structure. At higher frequencies, 30% of alignment sites experienced precise alignment and with almost no stray wires.

We have examined in a number of parameters including solution medium, signal frequency, electrode layer structure and planar electrode geometry. While our results are promising there is room for further optimization. A specific area that must be studied more closely is the fabrication and delivery of the nanowire suspension. In our experiments the suspensions were fabricated by sonicating nanowires from a substrate to suspend them in solution. This method was found to be very inconsistent offering little control over the in-solution nanowire lengths and solution densities despite seemingly similar conditions. Tighter control over both of these variables would assist in achieving more robust and reliable nanowire placement. In addition to improving the suspension itself, developing more controlled delivery method, perhaps using microfluidics, would also help by precisely controlling the volume and spatial

distribution of the solution above an alignment site. Furthermore advanced delivery techniques should also allow for the ability to quickly switch between suspensions of different types of nanowires allowing for the placement of a variety of nanowires in a single nanowire based system. Despite these shortcomings DEP has been shown to be an effective tool in the manipulation and placement of semiconductor nanowires.

Portions of this chapter have been submitted for publication, 2009, S. Raychaudhuri, S. A. Dayeh, D. Wang and E. T. Yu. The dissertation author is the first author of this paper.

References

- ¹ M. Law, J. Goldberger, and P. Yang, *Annu. Rev Mater. Res.*, **34**, 83 (2004).
- ² W. Lu and C. M. Lieber, *J. Phys. D: Appl. Phys.*, **39**, R387 (2006).
- ³ M. T. Björk, B. J. Ohlsson, C. Thelander, A. I. Persson, K. Deppert, L. R. Wallenberg, and L. Samuelson, *Appl. Phys. Lett.*, **81**, 4458 (2002).
- ⁴ J. Xiang, W. Lu, Y. Hu, Y. Wu, H. Yan, and C. M. Lieber, *Nature*, **441**, 489 (2006).
- ⁵ M. T. Björk, O. Hayden, H. Schmid, H. Riel and W. Riess, *Appl. Phys. Lett.*, **90**, 142110 (2007).
- ⁶ S. A. Dayeh, C. Soci, P. K. L. Yu, E. T. Yu, and D. Wang, *Appl. Phys. Lett.*, **90**, 162112 (2007).
- ⁷ Y. Hu, J. Xiang, G. Liang, H. Yan, C. M. Lieber, *Nano Lett.*, **8**, 925 (2008).
- ⁸ C. Thelander, L. E. Fröberg, C. Rehnstedt, L. Samuelson, and L.-E. Wernersson, *Elect. Dev. Lett.*, **29**, 206 (2008).
- ⁹ P. J. Pauzauskie and P. Yang, *Materials Today*, **10**, 36, (2006).
- ¹⁰ F. Qian, S. Gradecak, Y. Li, C.-Y. Wen, and C. M. Lieber, *Nano Lett.*, **5**, 2287 (2005).
- ¹¹ F. Qian, Y. Li, S. Gradecak, H.-G. Park, Y. Dong, Y. Ding, Z. L. Wang and C. M. Lieber, *Nature Materials*, **7**, 701 (2008).
- ¹² C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, J. Park, X.Y. Bao, YH. Lo, D. Wang, *Nano Lett.*, **7**, 1003 (2007).
- ¹³ C. J. Novotny, E. T. Yu, and P. K. L. Yu, *Nano Lett.*, **8**, 775 (2008).
- ¹⁴ Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science*, **293**, 1289 (2001).
- ¹⁵ M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, *Angew. Chem. Int. Ed.*, **41**, 2405 (2002).
- ¹⁶ Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, *Nano Lett.*, **4**, 245 (2004).

-
- ¹⁷ M. C. McApline, H. Ahmad, D. Wang and J. R. Heath, *Nature Materials*, **6**, 379 (2007).
- ¹⁸ F. Patolsky, B. P. Timko, G. Zheng, and C. M. Lieber, *MRS Bulletin*, **32**, 142 (2007).
- ¹⁹ F. Patolsky, B. P. Timko, G. Yu, Y. Fang, A. B. Greytak, G. Zheng, and C. M. Lieber, *Science*, **313**, 1100 (2006).
- ²⁰ W. Kim, J. K. Ng, M. E. Kunitake, B. R. Conklin, and P. Yang, *J. A. Chem. Soc.*, **129**, 7228 (2007).
- ²¹ B. Messer, J. H. Song, and P. Yang, *J. Am. Chem. Soc.*, **122**, 10232 (2000).
- ²² Y. Huang, X. Duan, Q. Wei, and C. M. Lieber, *Science*, **291**, 630 (2001).
- ²³ Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber **294**, 1313 (2001).
- ²⁴ F. Kim, S. Kwan, J. Akana, and P. Yang, *J. Am. Chem. Soc.* **123**, 4360 (2001).
- ²⁵ A. Tao, F. Kim, C. Hess, J. Goldberger, R. He, Y. Sun, Y. Xia, and P. Yang, *Nano Lett.*, **3**, 1229 (2003).
- ²⁶ D. Whang, S. Jin, Y. Wu, and C. M. Lieber, *Nano Lett.*, **3**, 1255 (2003).
- ²⁷ P. Yang, *Nature*, **425**, 243 (2003).
- ²⁸ G. Y. Jung, S. Ganapathiappan, X. Li, D. A. A. Ohlberg, D. L. Olynick, Y. Chen, W. M. Tong and R. S. Williams, *Appl. Phys. A*, **78**, 1169 (2004).
- ²⁹ A. Zhang, S. You, C. Soci, Y. Liu, D. Wang and Y.-H. Lo, *Appl. Phys. Lett.*, **93**, 121110 (2008).
- ³⁰ A. I. Hochbaum, R. Fan, R. He and P. Yang, *Nano Lett.*, **5**, 457 (2005).
- ³¹ H. J. Fan, W. Lee, R. Scholz, A. Dadgar, A. Krost, K. Nielsch and M. Zacharias, *Nanotechnology*, **16**, 913 (2005).
- ³² J. Motohisa, J. Noborisaka, J. Takeda, M. Inari and T. Fukui, *J. Cryst. Growth*, **272**, 180 (2004).
- ³³ L. E. Jensen, M. T. Bjrk, S. Jeppesen, A. I. Persson, B. J. Ohlsson, and L. Samuelson, *Nano Letters*, **4**, 1961 (2004).

-
- ³⁴ S. A. Dayeh, “Semiconductor Nanowires for Future Electronics: Growth, Characterization, Device Fabrication, and Integration”, Doctoral Dissertation, University of California San Diego (2008).
- ³⁵ P. A. Smith, C. D. Nordquist, T. N. Jackson, T. S. Mayer, B. R. Martin, J. Mbindyo, and T. E. Mallouk, *Appl. Phys. Lett.*, **77**, 1399 (2000).
- ³⁶ H. A. Pohl, Dielectrophoresis, Cambridge University Press: New York, NY (1978).
- ³⁷ T.B. Jones, Electromechanics of Particles, Cambridge University Press: New York, NY (1995).
- ³⁸ H. Morgan and N. G. Green, AC Electrokinetics: colloids and nanoparticles, Research Studies Press LTD: Baldock, Hertfordshire, England (2003).
- ³⁹ J. Venermo and A. Sihvola, *Journal of Electrostatics*, **63**, 101 (2005).
- ⁴⁰ K. Yamamoto, S. Akita and Y. Nakayama, *J. Phys. D: Appl. Phys.*, **31**, L34 (1998).
- ⁴¹ R. Krupke, F. Hennrich, H. B. Weber, D. Beckmann, O. Hampe, S. Malik, M. M. Kappes, and H. V. Löhneysen, *Appl. Phys. A*, **76**, 397 (2003)
- ⁴² C. K. M. Fung, V. T. S. R. H. M. Chan and W. J. Li, *IEEE Trans. on Nanotech.*, **3**, 395 (2004).
- ⁴³ J. Li, Q. Zhang, N. Peng, and Q. Zhu, *Appl. Phys. Lett.*, **86**, 153116 (2005).
- ⁴⁴ H.-W. Seo, C.-S. Han, D.-G. Choi, K.-S. Kim and Y.-H. Lee, *Microelectronic Engineering* **81**, 83 (2005).
- ⁴⁵ J. J. Boote and S. D. Evans, *Nanotechnology* **16** 1500 (2005).
- ⁴⁶ S. J. Papadakis, Z. Gu, and D. H. Gracias, *Appl. Phys. Lett.*, **88**, 233118 (2006).
- ⁴⁷ H. W. Seo, C.-S. Han, S. O. Hwang and J. Park, *Nanotechnology*, **17**, 3388 (2006).
- ⁴⁸ S. Kumar, S. Rajaraman, R. A. Gerhardt, Z. L. Wang, and P. J. Hesketha, *Electrochimica Acta*, **51**, 943 (2005).
- ⁴⁹ S. Rajaraman, H. (M.) Noh, P. J. Hesketh and D. S. Gottfried, *Sensors and Actuators B*. **114**, 392 (2006).

-
- ⁵⁰ C. S. Lao, J. Liu, P. Gao, L. Zhang, D. Davidovic, R. Tummala and Z. L. Wang, *Nano Lett.*, **6**, 263 (2006).
- ⁵¹ J. Suehiro, N. Nakagawa, S.-i. Hidaka, M. Ueda, K. Imasaka, M. Higashihata, T. Okada and M. Hara, *Nanotechnology*, **17**, 2567 (2006).
- ⁵² D. Wang, R. Zhu, Z. Zhou, and X. Ye, *Appl. Phys. Lett.*, **90**, 103110 (2007).
- ⁵³ T. H. Kim, S. Y. Lee, N. K. Cho, H. K. Seong, H. J. Choi, S. W. Jung and S. K. Lee, *Nanotechnology*, **17**, 3394, (2006).
- ⁵⁴ S.-Y. Lee, T.-H. Kima, D.-I. Suha, J.-E. Parka, J.-H. Kima, C.-J. Youna, B.-K. Ahnb and S.-K. Leea, *Physica E*, **36**, 194 (2007).
- ⁵⁵ A. Motayed, M. He, J. Melngailis and S. N. Mohammad, *J. Appl. Phys.*, **100**, 114310 (2006).
- ⁵⁶ X. Duan, Y. Huang, Y. Cui, J. Wang, C. M. Lieber, *Nature* **409**, 66, (2001).
- ⁵⁷ R. J. Hamers, J. D. Beck, M. A. Eriksson, B. Li, M. S. Marcus, L. Shang , J. Simmons and J. A. Streifer, *Nanotechnology*, **17**, S280 (2006).
- ⁵⁸ S. Evoy, N. DiLello, V. Deshpande, A. Narayanan, H. Liu, M. Riegelman, B.R. Martin, B. Hailer, J.-C. Bradley, W. Weiss, T.S. Mayer, Y. Gogotsi, H.H. Bau, T.E. Mallouk and S. Raman, *Microelectronic Engineering*, **75**, 31 (2004).
- ⁵⁹ A. Narayanan, Y. Dan, V. Deshpande, N. Di Lello, S. Evoy and S. Raman, *IEEE Trans. on Nanotech.*, **5**, 101 (2006).
- ⁶⁰ S.-Y. Lee, T.-H. Kim, D.-I. Suh, N.-K. Cho, H.-K. Seong, S.-W. Jung, H.-J. Choi, S.-K. Lee, *Chemical Physics Letters*, **427**, 107 (2006).
- ⁶¹ N. G. Green, A. Ramos, A. González, H. Morgan, and A. Castellanos, *Phys, Rev. E.*, **61**, 4011 (2000).
- ⁶² Dayeh, S. A.; Susac, D.; Kavanagh, K. L.; Yu, E. T.; Wang, D. *Adv. Func. Mat.* accepted for publication, 2009

Appendix A

Polydimethylsiloxane (PDMS) Preparation

Polydimethylsiloxane (PDMS) was used to fabricate a fairly simple cup-like structure to contain isopropyl alcohol-based nanowire solutions in section 3.2 of this dissertation. Furthermore PDMS can be used to construct micro-fluidic channels that could eventually be used to deliver nanowire solutions to DEP alignment sites in a highly controlled fashion. In this appendix we will discuss the basic method used to construct PDMS structures.

The structures used in this dissertation were constructed from a commercially available PDMS product line from Dow Corning called Sylgard 184. The product consists of a base chemical and a curing agent. To fabricate structures the base chemical and curing agent must first be mixed in a 10:1 ratio by weight. The mixture must be thoroughly stirred and then placed in vacuum (> 100 mTorr) for at least 45 minutes to remove any air pockets.

Next the mixture is poured over a Si wafer (which is mounted in the bottom of a plastic Petri dish) until the approximate desired PDMS thickness is achieved. In our experiments the PDMS layer used was several millimeters thick. The entire dish is then placed in an oven set at 55°C for at least 1 hour to allow the PDMS to cure. Once cured, the PDMS can be sliced into smaller pieces with a razor blade and peeled off

the surface of the Si wafer. PDMS “cups” were fashioned from these PDMS pieces of by simply punching a hole through the piece.

The PDMS cup must then be mounted to the DEP chip. The PDMS cup is first sonicated in IPA to remove any particles that may have collected on the PDMS surface. The PDMS piece is then placed on top of the DEP substrate such that the smooth side of the PDMS (the side that was facing the Si wafer during curing) is in contact with the DEP chip surface. The chip is then placed on a hot plate set to 105 °C for 30 minutes allowing the PDMS to form a weak, but liquid-tight bond with the SiO₂ surface of the chip. If necessary, a more permanent bond can be formed by treating the PDMS surface with UV/ozone prior to attaching it to the surface of the chip.

In this particular preparation a blank Si wafer was used to create a very smooth PDMS surface to bond with our DEP chip. It is possible to fabricate more complex micro-fluidic devices by using standard lithography techniques to etch a pattern into the Si Wafer. The wafer will then act as a mold allowing the creation of micro-fluidic channels in PDMS that can then be bonded to the surface of a DEP chip and be used to deliver nanowire solution to various points on a DEP chip.

Appendix B

DEP Electrode Fabrication

B.1 Introduction

The electrodes used to perform the precision DEP experiments in section 3.3 were fabricated at UCSD by the author of this dissertation. This appendix will provide a detailed description of the complete fabrication process used in the construction of these electrodes.

B.2 Wafer Preparation

Plasma enhanced chemical vapor deposition (PECVD) was used to deposit SiN_x on a 4 inch Si wafer in order to create a semi-insulating substrate on which to fabricate the DEP electrodes themselves. To do this the Oxford Plasmalab PECVD system was used. First, the system is pumped down for 10 minutes to thoroughly clear out the system of any contaminant gasses and to allow the stage and sample to stabilize at a temperature of 350 °C. Next N_2 is flowed at 2000 sccm with the chamber pressure held at 1000 mTorr for 1 minute to allow the temperature of the system to stabilize with gasses flowing and to further purge the system. Next, the actual

deposition is carried out by flowing SiH_4 , NH_3 , and N_2 at 400 sccm, 22 sccm and 600 sccm respectively, with the chamber pressure set to a pressure of 650 mTorr. The plasma power is set to 20 watts and is cycled between low freq (150 kHz) and high freq (13.56 MHz) for 7 and 13 second periods, respectively, for the duration of the deposition. Once the deposition time is reached the plasma power is turned off and the system is pumped and purged before removing the sample. The deposition is carried out for 43 minutes resulting in approximately 500 nm of SiN_x deposited on Si. The etch rate for PECVD deposited SiN_x is found to be 300 Å/minute in 6:1 BOE. Once the deposition is complete the wafer is cleaved into smaller pieces of 10 by 5 mm using by scribing the surface and breaking then breaking the sample along a straight edge.

B.3 Alignment Site Patterning and Metal Deposition

The alignment site electrodes and double bus bars are patterned by electron beam lithography using a converted JOEL JSM 6400 Scanning Electron Microscope controlled by NPGS pattern generation software to align and write patterns. Alignment marks are also written in this step to allow proper pattern alignment in later fabrication steps.

Prior to e-beam lithography the sample is cleaned by rinsing in acetone, methanol and isopropyl alcohol followed by 2 minutes in oxygen plasma (partial

oxygen pressure of 200 mTorr, power setting of 150 watts). These settings may not correspond to physical values, but are the settings used on the Technics PEIIB Planar Etch System in the nano3 facility at UCSD. Once the sample is cleaned PMMA 950 C4 resist is spun on the sample at a speed of 4000 RPM for 50 seconds. After spinning the sample is annealed on a hotplate for 90 seconds at 180 °C. The spun on layer of PMMA is measured to be around 270 nm using the Filmetrics F20.

A scribe is used to scratch the resist on each corner of the sample before the sample is loaded into the JSM 6400 system. Once the sample is loaded the stage is moved such that the beam is directed at the faraday cup so that it can be set to the appropriate values. The acceleration voltage is set to 30 kV, and the beam current is set to 50 pA. These settings result in very sharp features (1 μm lines have clearly defined edges and corners). The beam requires about 1 hour to warm up to maintain a stable beam current.

Once the beam is warm, measurements are made at each corner of sample to note the numerical value of the stage position at each corner of the sample as well as the focus value (found by focusing on the scratches in the resist at each corner). These values are then averaged to find the position and focus value at the center of the sample. The beam is then blanked, the stage is moved to the center position and the focus is set to the calculated value. The NPGS software is then used to write the pattern. The area dose used to achieve proper exposure is $300 \mu\text{C}/\text{cm}^2$ and the line-to-line and point-to-point spacing are both set to 27.25 nm. Once the sample has been exposed the samples are removed and developed in MIBK:IPA 1:3 developer for 90

seconds followed by a 30 second rinse in isopropyl alcohol. After development the sample is placed in the Technics PEIIB Planar Etch System (partial oxygen pressure of 200 mTorr, plasma power of 150 Watts) for 30 seconds to remove any residual PMMA in the pattern. Longer plasma treatments will result in damage to the pattern.

The samples is then loaded into the Temescal BJD-100 electron beam evaporator and pumped down until vacuum level of at least 7×10^{-8} Torr is achieved. A 10 nm Ti adhesion layer is then deposited at a rate no greater than 1 Å/sec followed by a 90 nm Au layer also deposited at a rate no greater than 1 Å/sec. After deposition the sample is left overnight in a beaker of acetone to dissolve the patterned PMMA and lift off excess metal. The samples is then removed from the beaker and a gentle spray of acetone is used to remove any remaining unwanted metal. If this is not sufficient light sonication can be used.

B.4 Probe Pad Patterning and Metal Deposition

Optical lithography is used to pattern large contact pads to allow easy probing to drive the alignment sites. The masks used for these pads are created in a relatively economical manner by having a commercial laser photo-plotting service (CAD Art Services, <http://outputcity.com>) transfer the pattern design to a transparency mask. The service is able to achieve resolution of 20,000 dpi which allows for a reasonable minimum feature size of $\sim 10 \mu\text{m}$. The transparency mask is then cut out and mounted

on a blank quartz mask plate. This is done by placing one small drop of water on the plate and then placing the transparency mask on the drop of water. The water spreads out between the mask and plate and firmly holds the two in close contact. Care must be used to make sure the correct amount of water is used. Too much water will result in poor adhesion allowing the transparency mask to move around the quartz plate.

The sample was once again prepared by rinsing in acetone, methanol and isopropyl alcohol, followed by 2 minutes of oxygen plasma in the Technics PEIIB Planar Etch System (partial oxygen pressure of 200 mTorr, power of 150 watts). Shiply S1805 photoresist is then spun on the sample for 40 seconds at 4000 RPM. The sample is then annealed on a hot plate for 60 seconds at 105 °C. The resist layer is expected to be approximately 500 nm thick.

Alignment and exposure are carried out in the Karl Süss MA6 mask aligner using hard contact mode. The sample is exposed for 4 seconds at 9 mW. The sample is then developed in Shiply MF319 or Shiply MF321 developer for approximately 20 seconds (10 seconds beyond the point that clouds of photoresist can be seen floating up of the surface of the sample). The sample is then rinsed in DI water. Electron beam evaporation is then used to deposit metal layers, followed by a lift off in acetone, exactly as described in section B.2.

B.5 Passivation Layer Fabrication

A passivation layer of SiO_2 is deposited across the entire surface of the sample using the Oxford Plasmalab PECVD. First, the system is pumped down for 10 minutes to thoroughly clear out the system of any contaminant gasses and to allow the stage and sample to stabilize at a temperature of 350°C . Next N_2 is flowed at 2000 sccm with the chamber pressure held at 1000 mTorr for 3 minute to allow the temperature of they system to stabilize with gasses flowing. This step is extremely important. Because there is now metal on the surface of the sample thermal gradients will exist and must be given time to stabilize. If this step is not long enough bubbles will form in the oxide above metalized areas. Next the actual deposition is carried out by flowing SiH_4 and N_2 at 170 sccm and 710 sccm respectively with the chamber pressure set to a pressure of 1000 mTorr. The plasma power is set to 20 watts at 13.56 MHz for the duration of the deposition. Once the deposition time is reached the plasma power is turned off and the system is pumped and purged before the sample is removed. The deposition is carried out for 3.22 minutes resulting in approximately 250 nm of SiO_2 deposited on surface. The etch rate of PECVD deposited SiO_2 is found to be 3300 Å/minute in 6:1 BOE.

Once the passivation layer has been deposited windows must be opened in to access the probe pads and alignment sites. The probe pad windows are defined using optical lithography and the alignment site windows are defined using electron beam lithography.

The sample was once again prepared by rinsing in acetone, methanol and isopropyl alcohol followed by 2 minutes of oxygen plasma in the Technics PEIIB Planar Etch system (partial oxygen pressure of 200 mTorr, power of 150 watts). Shiply S1818 photoresist is then spun on the sample for 40 seconds at 4000 RPM. The sample is then annealed on a hot plate for 60 seconds at 105 °C. The resist is expected to be approximately 1.8 μm thick.

Alignment and exposure are carried out in the Karl Süss MA6 mask aligner using hard contact mode. The sample is exposed for 24 seconds at 9 mW. The sample is then developed in Shiply MF319 or Shiply MF321 developer for approximately 20 seconds (10 seconds after the time that clouds of photoresist can be seen floating up of the surface of the sample). The sample is then rinsed in DI water. After development the sample is once again annealed on a hot plate for 60 seconds at 105 °C. The purpose of this second anneal is to strengthen the patterned photoresist and make it more resistant to wet etching.

The actual removal of the oxide is done by placing the sample in 6:1 BOE (buffered oxide etch) for 55 seconds followed by a rinse in DI water. Because of the difference in etch rates between SiO_2 (3300 $\text{\AA}/\text{min}$) and SiN_x (300 $\text{\AA}/\text{min}$) over etching is not a significant issue.

Electron beam lithography is used to define openings at each alignment site which are then etched using the a 55 second etch in 6:1 BOE. The patterning is done using the exact same e-beam lithography process described in section B.2

Appendix C

Alignment Site Modeling Using COMSOL

The DEP alignment sites discussed in sections 3.3 and 3.4 of this dissertation were modeled using finite element analysis to better understand the nature of the electric field around each alignment site, and consequently the nature of the DEP force on particles in close proximity to an alignment site. In this appendix we discuss details of the COMSOL model used to study alignment sites.

Four alignment site geometries were considered using COMSOL including an alignment site with double bus bars separated by 100 μm , an alignment site with double bus bars separated by 50 μm , an alignment site with single bus bars separated by 100 μm and finally, an alignment site with single bus bars separated by 50 μm . For illustrative purposes we will present a detailed description of the two models for alignment sites with 50 μm bus bar spacing. The model geometries can simply be adjusted to accommodate alignment sites with 100 μm bus bar spacing.

Figures C.1 and Figure C.2 shows the 3-dimensional physical models that were used to calculate the electric field for alignment sites with double and single bus bars, respectively. The sub-domain parameter settings for the volume below an alignment site was set to values appropriate for SiN_x while the volume above an alignment site was set to values appropriate for de-ionized water. The regions and parameter values for SiN_x and de-ionized water are shown in Figures C.3 and C.4.

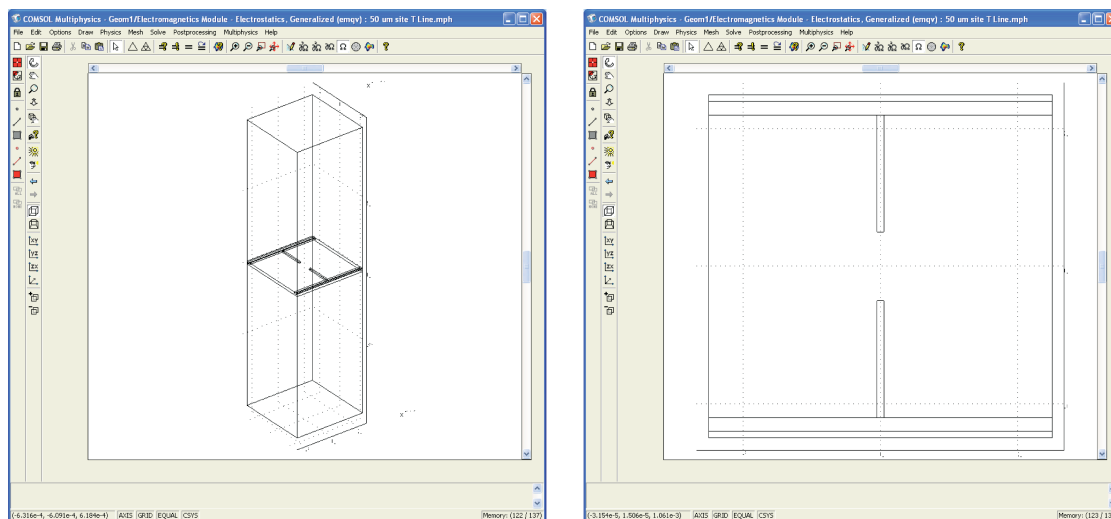


Figure C.1

COMSOL windows showing 3 dimensional view (left) and top view (right) of the double bus bar alignment site model with $50\ \mu\text{m}$ spacing. Periodic boundary conditions are used to simulate the double bus bar effect.

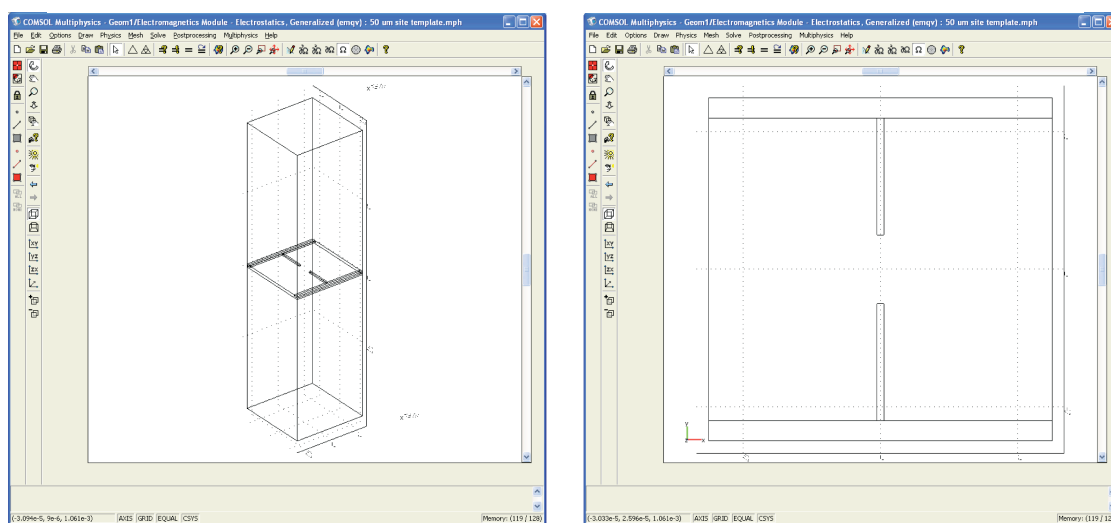


Figure C.2

COMSOL windows showing 3 dimensional view (left) and top view (right) of the single bus bar alignment site model with $50\ \mu\text{m}$ spacing.

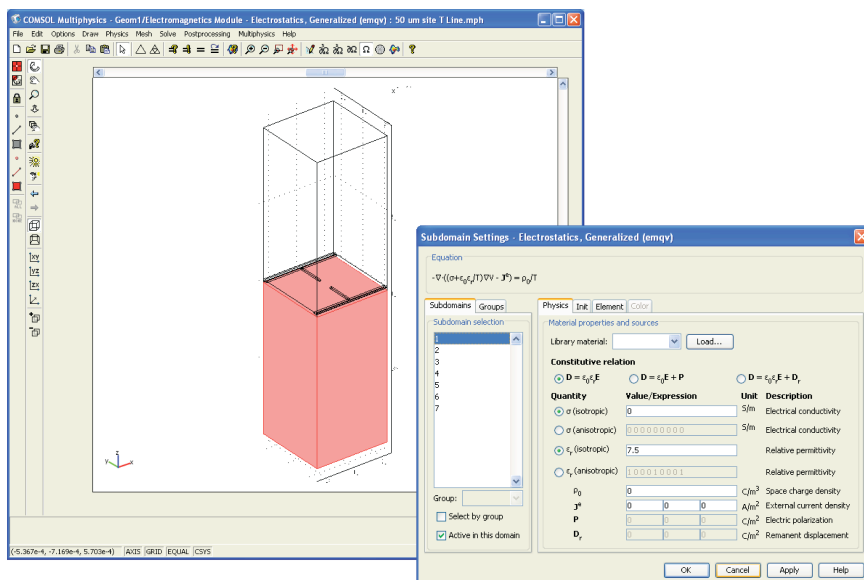


Figure C.3

Alignment site model with SiN_x region highlighted (left) and SiN_x region parameter values (right).

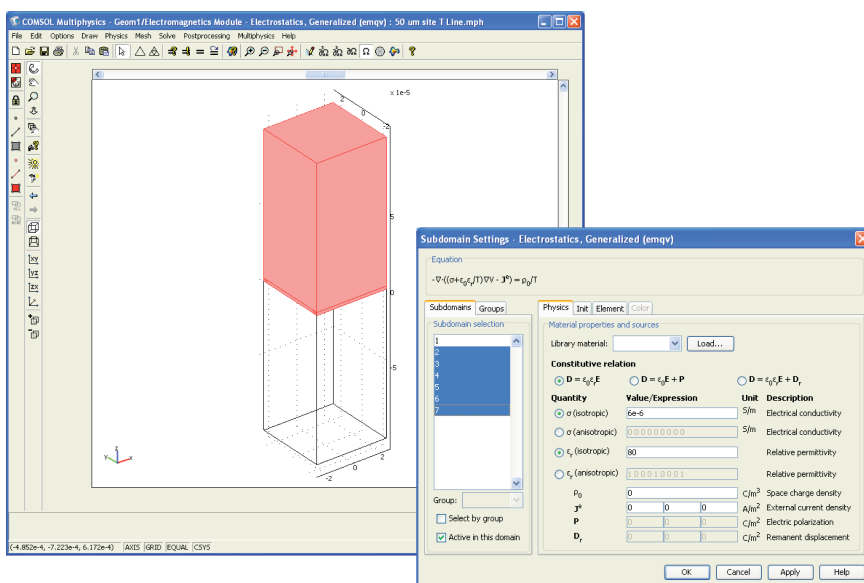


Figure C.4

Alignment site model with de-ionized water region highlighted (left) and de-ionized water region parameter values (right).

In order to calculate the electrostatics associated with an alignment site it is necessary to apply the appropriate boundary conditions. The electrode surfaces, shown in Figure C.5, must be set to voltage potentials of positive and negative 5 volts. The boundary surface above and below the electrodes, shown in figure C.6 are set to ground, but are sufficiently far from the alignment site that they have little impact on simulation. The boundary surfaces around the alignment site are all set to be perfect insulators which as shown in Figure C.7. In the case of double bus bar, two surfaces (shown in figure C.8) must additionally be set to have periodic boundary conditions. Figures C.7 and C.8 show boundary conditions which are sufficient to allow these simulations to represent an array of alignment sites.

The calculation is carried out using an extra fine mesh. Arrow plots are utilized in order to view the electric field, as shown in Figure C.9. Slice plots are used to view the magnitude of the electric field gradient, squared, as shown in Figure C.10, which corresponds to the magnitude of the DEP force.

By examining the outputs of these simulations it is possible to better understand the electrostatics associated with the particular alignment site geometries and as a result, the DEP force acting on particles in the vicinity of the alignment site.

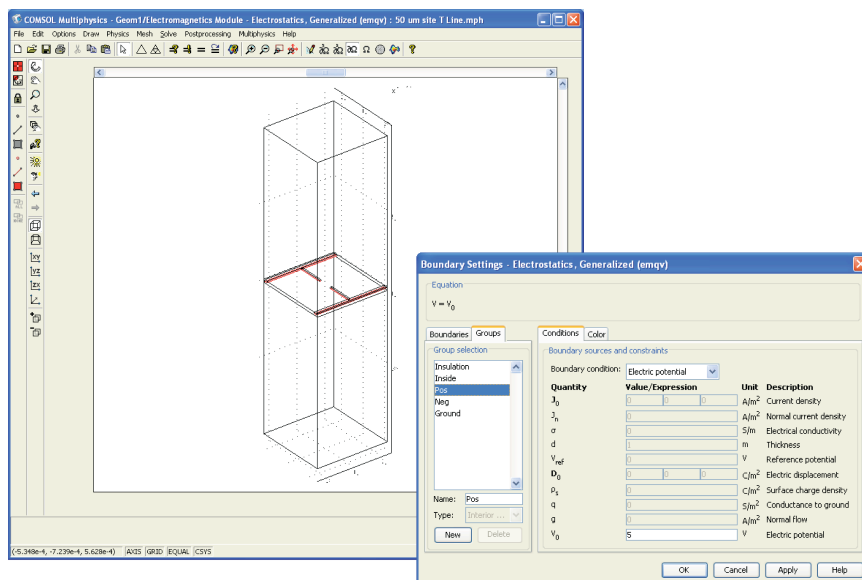


Figure C.5

Alignment site model with electrode boundaries highlighted (left) and boundary parameter values for the positive electrode (right).

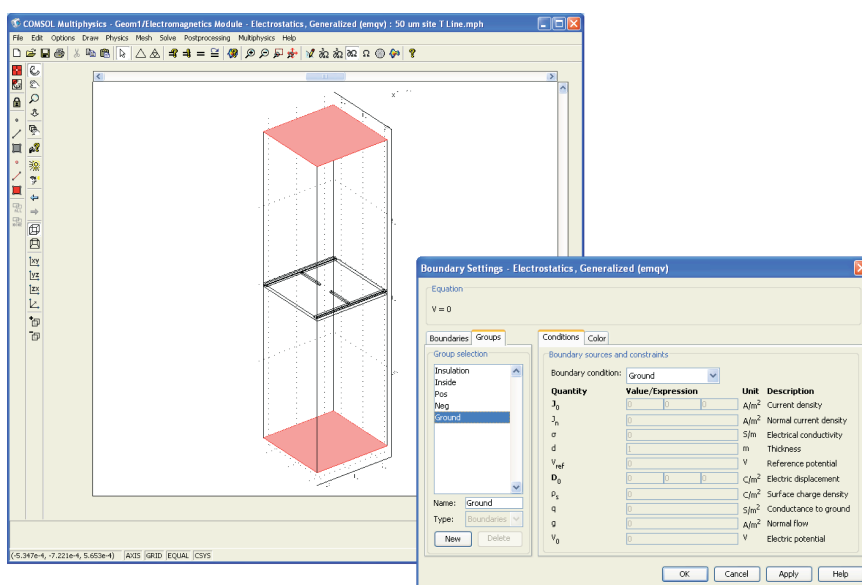


Figure C.6

Alignment site model with upper and lower boundaries highlighted (left) along with their corresponding boundary parameter values (right).

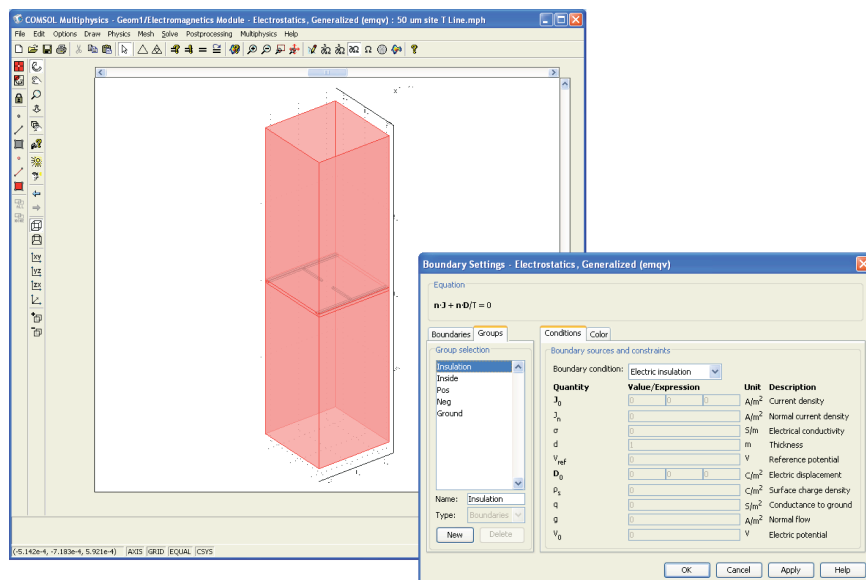


Figure C.7

Alignment site model with surrounding boundaries highlighted (left) along with their corresponding boundary parameter values (right).

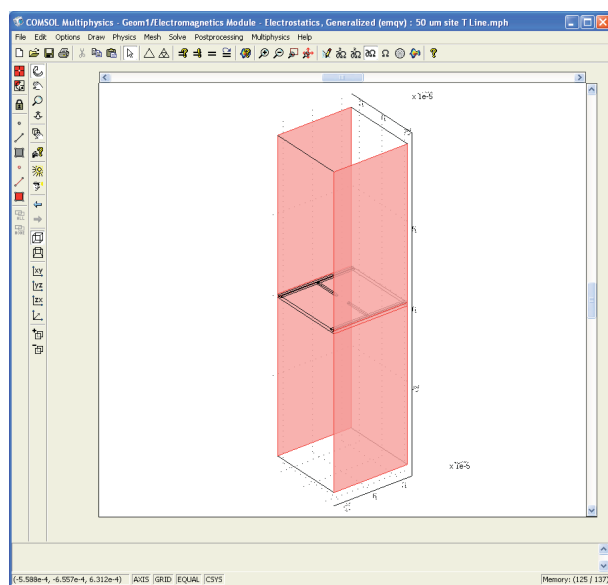


Figure C.8

Alignment site model with boundaries that are parallel to the double bus bars highlighted. These boundaries are set to be periodic to effectively model the double bus bar architecture.

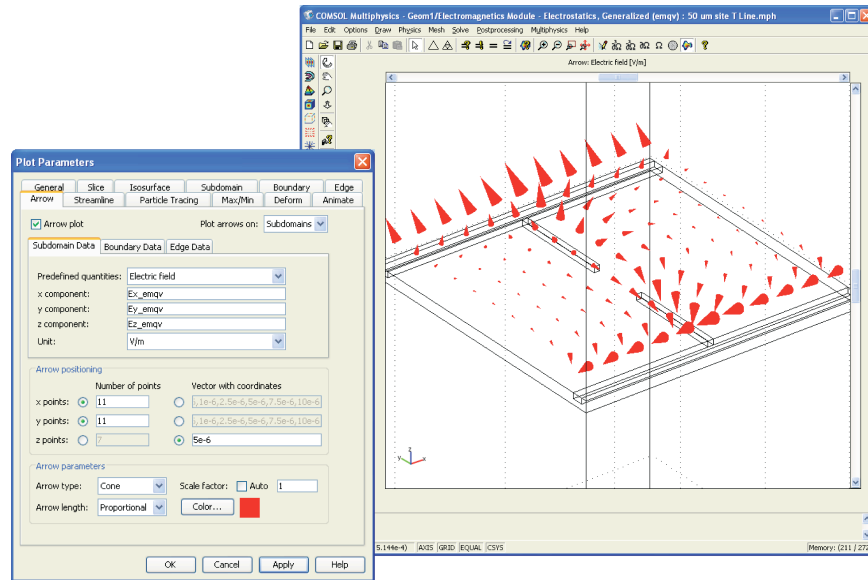


Figure C.9

Alignment site model showing a 3 dimensional arrow plot of the electric field $5 \mu\text{m}$ above an alignment site along with its corresponding plot parameter values (left).

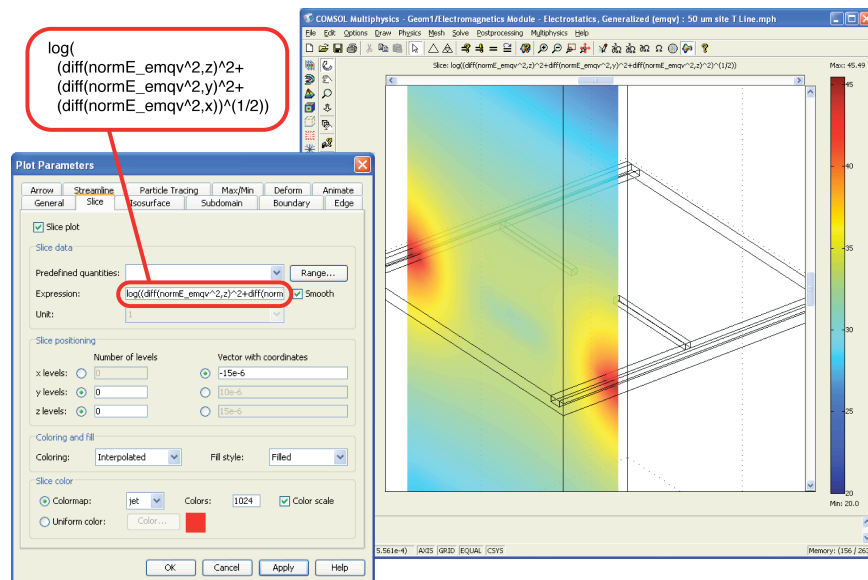


Figure C.10

Alignment site model showing a slice plot along the y-z plane of the magnitude of the electric field, squared, on a log scale, $15 \mu\text{m}$ away an alignment site along with its corresponding plot parameter values (left).