Advances in Crystal Growth and 
Assembly for Imparting Novel Photonic 
Properties to Semiconductor Nanowires

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Advances in Crystal Growth and Assembly for Imparting Novel Photonic Properties to Semiconductor Nanowires

A dissertation presented
by
Max Nathan Mankin
to
The Department of Chemistry and Chemical Biology
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Chemistry
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Advances in Crystal Growth and Assembly for Imparting Novel Photonic Properties to Semiconductor Nanowires

Abstract

Semiconductor nanowires comprise a versatile materials platform with which to characterize the properties of nanomaterials. The vast range of structural and compositional diversity of nanowires has also enabled their use as low-footprint building blocks in a variety of applications including bioelectronics, photonics, and energy conversion. Synthetic control of nanowire size, morphology, and composition as well as assembly of nanowires into predetermined positions and orientations are paramount to enabling the aforementioned fundamental and applied research. To this end, this thesis presents original research on four aspects of semiconductor nanowire synthesis and assembly, with emphasis on material characterization and how advances in synthesis and assembly can impart new photonic properties to nanowires.

First, I demonstrate facet-selective epitaxial growth of compound semiconductors on silicon nanowires. Electron microscopy and growth studies suggest that facet-selective formation of an oxide prevents growth of the compound semiconductor on certain facets. Facet-selective epitaxy is general to several compound semiconductor materials and for micro-to-mesoscale wires. Optical characterization shows that facet-selective epitaxy integrates the photonic properties of compound semiconductors with silicon nanowires.
Next, I discuss a crystal growth phenomenon unique to one-dimensional materials that combines Plateau-Rayleigh instability with nanowire shell growth to yield diameter-modulated nanowires. We demonstrate wide synthetic tunability over diameter-modulated nanowire morphologies and compositions. Growth studies suggest that surface energy reductions drive the formation of periodic shells, and that kinetic control of growth enables this tunability. Finally, we show that diameter-modulated nanowires display unique optical properties compared to uniform diameter nanowires.

Third, I present an assembly technique that incorporates positioning and shaping to yield U-shaped nanowires with >90% yield and positioning accuracy within 10s of nanometers over a wafer scale. Shape-controlled assembly involves patterning shaped trenches and then shear transferring nanowires to the patterned substrate wafers, where the trenches define the positions and shapes of transferred nanowires. We assemble U-shaped nanowire directional optical couplers that function as nanoscale photonic circuit elements.

Finally, I present optical studies of strained, U-shaped germanium nanowires. Light emission from single germanium nanowires is (i) localized to the strained portions of the nanowires, (ii) enhanced by factors >25 compared to unstrained segments of the nanowires, and (iii) can be monotonically tuned from ~1550 to 1900 nm by deterministically adjusting the radius of curvature and/or the diameter of the nanowires. These studies show that tuning assembly parameters to adjust strain in the nanowires yields changes to the nanowires’ electronic structure, and correspondingly, their optical properties.

Facet-selective epitaxy, Plateau-Rayleigh crystal growth, and shaped nanowire assembly afford exciting opportunities for (i) characterizing unique crystal growth modes of nanomaterials,
(ii) imparting novel morphological and crystallographic properties to nanowires, and (iii) studying relationships between these properties and the photonic attributes of nanostructures.
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List of Abbreviations

BHF: buffered hydrofluoric acid

CB: conduction band

CCD: charge-coupled device

CVD: chemical vapor deposition

CW: continuous wave

D: diameter

DRIE: deep reactive ion etching

ε: strain

EBL: electron beam lithography

EDS: energy dispersive x-ray spectroscopy

FIB: focused ion beam

FDTD: finite difference time domain

FFT: fast Fourier transform

FWHM: full width at half maximum

GOI: germanium-on-insulator

HRTEM: high resolution transmission electron microscope

IPA: isopropanol

IR: infrared

LED: light-emitting diode

µm: micrometer
N.A.: numerical aperture
NIR: near infrared
nm: nanometer
NP: nanoparticle
NW: nanowire
MMA: methyl methacrylate
PL: photoluminescence
PMMA: polymethyl methacrylate
P-R: Plateau-Rayleigh
ρ: radius of curvature
SA: surface area
SAE: selective area epitaxy
SAG: selective area growth
SAED: selected area electron diffraction
sccm: standard cubic centimeter per minute
s.d.: standard deviation
SE: surface energy
SEM: scanning electron microscope
STEM: scanning transmission electron microscope
TEM: transmission electron microscope
UV: ultraviolet
VB: valence band

VLS: vapor-liquid-solid
Chapter 1: Introduction

1.1 Nanoscience and nanotechnology

Nanoscience is the study of matter whose dimensions range from 1-1000 nanometers (nm; $10^{-9}$ meters) (1). The last several decades have witnessed an explosion of scientific and applied research on nanomaterials for several reasons. First, materials at the nanoscale often display properties which differ dramatically from their bulk or macroscale counterparts. For instance, since nanomaterials have extraordinarily high surface to volume ratios, they often display size-dependent melting points (2), catalytic activity different or enhanced relative to extended planar surfaces (3,4), as well as electronic (5,6) and optical (7) properties that closely depend on their surface chemistry and functionalization. Moreover, the characteristic length scales for many physical phenomena, such as electronic transport (8), optical absorption and scattering (9), thermal conduction (10), crystallographic defect propagation (11,12), and adatom diffusion lengths (Chapter 3) are on the nanoscale (1,13,14). As the dimensions of matter become comparable to these characteristic length scales, quantization effects can drastically alter the properties of nanomaterials as a function of their size and morphology (1, 13, 14).

Second, the small masses, volumes, and area footprints of nanomaterials enable current and future technologies. For instance, electronics embody one ubiquitous example of nano-enabled technologies; as consumer devices require more computing power but lower footprints, masses, and power consumption, semiconductor companies have been “cramming” more components into smaller chip areas (per Moore’s Law) (15). In particular, at the time of this writing, characteristic channel lengths in state-of-the-art transistor channels from Intel, Samsung, and ARM belong to the “14 nm node,” meaning that the smallest feature of single integrated
circuit components is \(~14\) nm (16). Processors featuring 10 nm features are projected to be commercially available starting in 2017 (17) and IBM recently (July, 2015) demonstrated a chip featuring 7 nm features (18). Moreover, the dimensions of nanomaterials are inherently on the scale of features within biological systems (e.g. cells, subcellular organelles, etc.). Therefore, emerging therapeutic and explorative technologies, such as bioelectronics (19) and nanoparticle-based therapeutics (20), incorporate nanoscale building blocks whose sizes enable them to readily interface with biological systems.

1.2 Synthesis of nanomaterials

The properties of nanomaterials depend strongly on their dimensions, morphologies, and surface properties (Section 1.1). Therefore, controlling and understanding nanomaterial synthesis affords rich opportunities to study novel material properties and to programmatically design nanomaterials for specific applications. Nanomaterials are typically synthesized through two paradigms known as “top-down” and “bottom-up” synthesis (21). Top-down synthesis can be explained by analogy to a sculptor chipping away at a large block of stone to produce a statue. In this case, nano- or microscale features are patterned, etched, milled, and/or deposited on a macroscopic starting material. Controlled top-down processes – known as nano- or microfabrication – form the basis of electronics manufacturing in the semiconductor industry, since these processes are scalable and often repeatable. However, current state-of-the-art top-down fabrication requires complex and expensive fabrication equipment and facilities and struggles to reliably pattern features with sizes below 100 nm (22).

In contrast, the assembly of construction materials into buildings serves as an excellent analogy for the additive process of bottom-up synthesis of nanomaterials, in which precursor atoms, molecules, or other building blocks are assembled, reacted, or otherwise bound together
to form nanomaterials (23). Examples of bottom-up synthesis include the growth of crystalline nanoparticles (24,25) and carbon nanotubes (26) from constituent atoms or molecular precursors. The advantages of bottom-up synthesis include fine control of the chemical properties of the products and the fact that most bottom-up procedures do not require equipment nearly as complex as that required for microfabrication. However, in contrast to top-down fabrication, scaling up of bottom-up syntheses remains challenging for many classes of nanomaterials.

Additionally, the products of bottom-up nanomaterial syntheses are often synthesized in a random orientation, or suspended in a solvent; this fact presents advantages and disadvantages. For cases in which nanomaterials need to be evenly dispersed across a substrate, suspensions in solvents are excellent precursors for final products or devices. As one example, quantum dot-based light emitting diodes (LEDs) and displays are fabricated by spin coating or drop casting colloidal solutions of quantum dots onto electrodes (27). However, when the spatial location of nanostructures is important (e.g. an electronic device whose electrical contacts must address a nanostructure in a specific location), precise positioning of randomly oriented nanomaterials has presented difficulties – and corresponding research opportunities – in the formation of integrated nano-devices (28). Advances in the assembly of randomly oriented 1D nanomaterials will be discussed further in Section 1.5 and Chapters 4 and 5.

1.3 Classification of nanomaterials

Nanomaterials are typically classified according to which of their characteristic length scales (x, y, or z) are larger than nanoscale (1). Nanoparticles, or zero-dimensional (0D) clusters, have nanometer-scale dimensions in x, y, and z (25). Examples include quantum dots and metal nanoparticles. Materials which are long in one dimension but nanoscale in the other two are known as one-dimensional (1D). Nanowires (NWs) (13) and nanotubes (26) are examples of 1D
structures. Finally, two-dimensional (2D) materials are extended in two dimensions, but nanoscale in the third (29). Examples of 2D materials include single or few layer graphene, hexagonal boron nitride, and layered chalcogenide compounds.

1.4 Bottom-up synthesis of nanowires

This thesis describes my research on novel bottom-up synthesis, assembly, and characterization of semiconductor NWs. Semiconductor NWs are of interest since they present a variety of unique characteristics useful to fundamental and applied science such as extraordinary tolerance for mechanical bending and deformation, large surface area to volume ratios, unique optical properties due to their subwavelength diameters, and their ability to be integrated with electronic devices and biological systems by serving as both active device elements and electrical or optical interconnects (13,21,23,28). The properties of NWs depend on parameters including composition, dopant profile, length, diameter, cross sectional morphology, and surface functionalization (Section 1.1). Accordingly, a vast body of research has focused on understanding and controlling the mechanisms of NW synthesis and on producing novel NW morphologies and compositions.

Bottom-up NW synthesis primarily involves two distinct growth modes: (1) axial elongation and (2) radial over-coating, as shown schematically in Figure 1.1 (13,21,23,28). Axial NW synthesis involves growth of material only at one end of a NW and not on the NW sidewalls, thereby elongating the NW. The vapor-liquid-solid (VLS) growth mechanism, which was first reported by Wagner and Ellis at Bell Labs in 1964 (30), constitutes the most common synthetic strategy for bottom-up axial elongation of NWs (Figure 1.1A). In the VLS NW growth mechanism, a vapor-phase precursor is decomposed on and subsequently dissolved in a metal catalyst particle at high temperature, forming a liquid eutectic. As additional precursor dissolves
in the catalyst particle, the concentration of the solute reaches a critical concentration in the droplet at which the precursor nucleates as a solid crystal (31,32).

The VLS technique for bottom-up NW synthesis is versatile and has been used to produce NWs with a variety of compositions, sizes, dopant profiles, and morphologies (31). For instance, one can predict proper conditions for NW synthesis simply by examining phase diagrams of the NW and catalyst material systems (31). Accordingly, the VLS mechanism has been successfully applied to synthesize a variety of semiconductor NW compositions (21,33). Moreover, tuning the diameter of the metal catalyst particle tunes the diameter of the NWs (34-36). Dopants can be incorporated into the NWs by supplying impurity-containing precursors during NW elongation (37). Since NWs grow axially, the precursors fed into a reactor can be adjusted with time to yield NWs whose properties (e.g. composition, dopant profile, dopant concentration, and even diameter) are modulated along the growth direction (38; additional references in Chapter 3; Figure 1.1B). Additional approaches to bottom-up NW growth (39) include the vapor-solid-solid (40) and solution-liquid-solid (41,42) mechanisms.

**Figure 1.1** Schematics depicting modes of bottom-up NW synthesis. For illustrative purposes, these schematics depict Si NW synthesis by chemical vapor deposition (34), but similar mechanisms apply to the synthesis of many materials (21, 31, 33). (A) VLS growth of Si NWs using an Au nanoparticle catalyst and a gaseous Si precursor. (B) Axial modulation of dopant concentration during Si NW elongation by supplying different precursor sources with time. (C)
**Figure 1.1, Continued:** Radial modulation to yield core/shell Si NWs by transitioning from growth conditions which promote axial elongation to those which promote conformal material deposition. In (B) and (C), boron- (phosphorous-) containing gaseous precursors yield p-type (n-type) doped Si.

In contrast, adjusting growth conditions to promote deposition of material conformally on NW sidewalls yields radial growth (Figure 1.1C); the resultant structures are known as “core/shell” NWs (43). Modulation of precursors during shell synthesis can generate NWs with various composition and dopant profiles in the radial direction (43,44). Various deposition methods have been demonstrated to synthesize a range of core/shell NW structures including chemical vapor deposition (43), atomic layer deposition (45), solution-phase/chemical bath deposition (46), and ion exchange (47). Shell growth is another effective tool for introducing new properties to NWs and enabling new applications, as discussed further in Section 1.6. Additional references related to NW shell growth will be reviewed in Chapters 2 and 3.

**1.5 Assembly of nanowires synthesized by bottom-up methods**

NWs must be programmatically oriented and positioned for use in devices. However, NWs that are grown by the VLS mechanism are often randomly oriented on a substrate (Section 1.4) in what is known as a NW ‘forest’ (Figure 1.2A and Appendices 1, 5, 18, and 24). Therefore, assembly methods are required to position and orient NWs grown by bottom-up methodologies (28,48). A variety of methods for NW assembly have been demonstrated, including alignment using electric fields (49,50), flowing fluids (51), bubbles (52), the Langmuir-Blodgett technique (53), and selective DNA interactions (54).
**Figure 1.2** Assembly of randomly oriented NWs. (A) Scanning electron microscope image of a randomly oriented “forest” of Si NWs (diameters ~ 100 nm) on a growth substrate. The NWs were synthesized by the Au nanoparticle-catalyzed VLS mechanism (see Appendices 1, 5, 18, and 24). Scale bar, 10 μm. (B) Schematic illustration of shear transfer assembly of NWs. Following NW synthesis, the growth substrate (gray, left) with a forest of NWs (blue) is placed in contact with a receiving substrate (green, right) with controlled downward pressure (P, orange) oriented normal to both substrates. Next, the growth substrate is translated (purple arrow) with respect to the receiving substrate.

Shear transfer is one of the most promising and scalable techniques for NW assembly (55). In this technique, a randomly oriented NW forest on a growth substrate is placed on a receiving substrate with controlled pressure and translated linearly along the receiving substrate (Figure 1.2B). The in-plane shear force attributed to friction from the linear motion of the growth substrate aligns the NWs (56). NW positions and orientations are set deterministically by chemically functionalizing and/or lithographically patterning the receiving substrate with chemically distinct surface regions to control the strength of the interaction between the NW and receiving substrate surface regions (55,57-59). However, one limitation of the initial reports of NW shear transfer assembly (55-59) is that the position of the NWs along the transfer direction cannot be well-defined. “Nanocombing” overcomes this limitation (60). In this technique, lithography and surface chemical functionalization are used to pattern a narrow window on the
receiving substrate that is adhesive to NWs. The area surrounding the attractive window is functionalized with a polymer layer whose surface is less adhesive to the NWs. Therefore, during transfer, NWs adhere to the window but are drawn out across the less adhesive region into highly aligned arrays with anchoring positions well-defined by the location of the adhesive windows.

1.6 Nanowire photonics and optoelectronics

There is significant fundamental and technological interest in the photonic and electro-optical properties of NWs. Excellent overviews of NW photonics are presented in several reviews (21,28,44,61-64) that discuss the properties and applications NW-based waveguides, lasers, LEDs, photodetectors, photovoltaics, non-linear optical elements, etc. Therefore, a detailed description of the vast field of NW photonics will not be reproduced here. However, this section reviews two specific bodies of excellent research that (i) preceded and partially inspired much of the work in this thesis, and (ii) particularly highlight how advances in NW synthesis and assembly can enable novel NW photonic properties and capabilities. First, developments in Si NW shell growth have enabled detailed characterization of horizontal single Si NWs configured as photovoltaics (65,66). These NW solar cells show promise for characterizing the fundamentals of light absorption in nanomaterials as well as low-footprint power sources for other nanoelectronics. The synthesis of radially doped p/i/n Si core/shell NWs (with nanocrystalline Si shells) enabled the first demonstration of bottom-up core/shell NW photovoltaic elements whose light conversion efficiencies were high enough to power other nanoscale electronics (67). Later, advances in Si NW shell synthesis yielded highly crystalline doped Si shells (68). When configured as photovoltaic devices, these highly crystalline core/shell NWs showed improved open circuit voltages and leakage currents relative to the earlier devices with nanocrystalline shells. Finally, additional synthetic control over the cross-sectional morphology (e.g. hexagonal
vs. rectangular) of these NW absorbers afforded extraordinary tunability over the optical absorption modes in these NWs (9,69).

Second, fluid flow-directed assembly (51) of crossed semiconductor NWs has enabled unique architectures for nanoscale photonic devices. Electrical measurements indicated that the crossed NW pairs form junctions at their interface. Thus, assembling NWs with a variety of dopants and compositions provides a versatile toolbox of potential crossed NW junctions which can be explored for device fabrication. For instance, crossed Si and CdS NWs form a heterojunction; in reverse bias, this junction acts as a sensitive, spatially localized avalanche photodetector with sensitivity primarily localized to within < 250 nm of the junction (70). Additionally, injecting charge carriers from Si NWs into compound semiconductor NWs with direct bandgaps (e.g. GaN, CdS, CdSSe, CdSe, and InP) produced light emission from the crossed NW junctions at energies equal to the bandgap of the compound semiconductor NW (71).

The above examples demonstrate that a detailed understanding of NW synthesis and advances in NW assembly enable new photonic applications such as ultra-small photovoltaic power sources, photodetectors, and LEDs. Additional specific motivations for imparting novel photonic properties to NWs will be discussed in more detail in the following chapters.

1.7 Presentation and scope of thesis

This thesis presents the results of my research studying and developing novel synthesis and assembly methods of semiconductor NWs, with an emphasis on advanced materials characterization and imparting novel photonic properties to NWs. To this end, Chapters 2 and 3 detail new modes of NW shell growth which yield novel NW morphologies and characterization.
of the new morphologies’ optical properties. Specifically, Chapter 2 discusses a novel mode of NW shell synthesis known as “facet-selective epitaxy” in which compound semiconductors grow epitaxially on specific facets of Si NWs. Growth studies and state of the art electron microscopy characterization suggest that selective oxidation of particular Si surface facets prevents growth on these facets to yield facet-selective growth. Additional synthesis experiments show that the technique is general to NWs of various sizes and to several compound semiconductor shell materials. Lastly, optical imaging and spectroscopy indicate that the facet-localized compound semiconductor material is of high optical quality, suggesting that facet selective epitaxy on 1D Si nano- and mesoscale-structures could serve as a unique platform for integrating compound semiconductors with group IV materials in (opto)electronics.

Chapter 3 presents an advance in NW synthesis which combines shell growth with the underlying physics of Plateau-Rayleigh instability to generate NWs with periodically diameter-modulated shells. Thus, this method is termed “Plateau-Rayleigh crystal growth.” Adjusting the synthetic shell deposition conditions enables rational tuning of the pitches of diameter modulation and the cross-sectional aspect ratios of the NWs. The results of growth studies as well as geometrical modeling suggest that (i) surface energy reductions drive the formation of diameter modulated periodic shells rather than uniform diameter shells and (ii) that Plateau-Rayleigh crystal growth is unique to 1D materials. Optical simulations indicate that these diameter-modulated Si NWs possess distinct absorption modes in the infrared region of the electromagnetic spectrum; the absorption modes supported by diameter modulated NWs are unique compared to those of Si NWs of uniform diameter. Thus, Chapters 2 and 3 show that both facet-selective epitaxy and Plateau-Rayleigh crystal growth serve as unique, versatile, and powerful synthetic platforms for imparting novel photonic capabilities to Si NWs.
The second half of this thesis (Chapters 4 and 5) presents a novel technique which combines NW assembly and shaping, as well as characterization of the resulting photonic properties of the assembled NWs. Chapter 4 details the new assembly concept which combines shear transfer NW assembly (Section 1.5) with lithographically patterned templates on the receiving substrate to simultaneously and deterministically control the positions, shapes, and orientations of NWs. Assembly trials demonstrate that NWs can be assembled into U-shapes with positions defined on a wafer scale with 10s of nanometer accuracy in the x-y (substrate) plane. Spectroscopic and electron microscopy characterization show that shaping yields primarily elastic deformation of the NWs. Further assembly studies suggest that the mechanism of NW shaping consists of (i) NWs anchoring on the templates on the receiving substrate followed by (ii) bending to conform to the template and (iii) alignment due to the in-plane shear force during assembly. Last, waveguiding studies of deterministically assembled U-shaped NWs demonstrate that the assembled NWs can serve as directional nanophotonic couplers, and more generally, as integrated nanoscale photonic circuit elements.

Finally, Chapter 5 further investigates the assembly and characterization of U-shaped NWs, using Ge NWs as a materials platform for investigating the effect of shaping-induced strain on the NWs’ optical properties. Raman spectroscopy studies and geometric analysis suggest that assembly of NWs into U-shapes imparts compressive and tensile strain on the inner and outer edges of the curved NWs, respectively. Photoluminescence imaging of single strained Ge NWs reveals strong near infrared light emission that is localized to the strained portions of the NWs and that is enhanced by factors greater than 25 compared to unstrained segments of the NWs. Spectroscopy shows that this emission can be monotonically tuned over 150 meV by deterministically adjusting the parameters of NW synthesis and/or shaped NW assembly.
Chapter 5 presents the first demonstration of using deterministic assembly and shaping to tune the intrinsic optical properties of NWs. Together, Chapters 4 and 5 demonstrate that advances in assembly of NWs can tune the photonic properties of semiconductor NWs.

1.8 References

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Chapter 2: Facet-selective epitaxy of compound semiconductors on faceted silicon nanowires

[The following chapter is derived in part from M. N. Mankin et al. Nano Letters 15, 4776-4782 (2015).]

Integration of compound semiconductors with silicon (Si) has been a long-standing goal for the semiconductor industry, as direct band gap compound semiconductors offer, for example, attractive photonic properties not possible with Si devices. However, mismatches in lattice constant, thermal expansion coefficient, and polarity between Si and compound semiconductors render growth of epitaxial heterostructures challenging. Nanowires (NWs) are a promising platform for the integration of Si and compound semiconductors since their limited surface area can alleviate such material mismatch issues. Here, we demonstrate facet-selective growth of cadmium sulfide (CdS) on Si NWs. Aberration-corrected transmission electron microscopy analysis shows that crystalline CdS is grown epitaxially on the \{111\} and \{110\} surface facets of the Si NWs but that the Si\{113\} facets remain bare. Further analysis of CdS on Si NWs grown at higher deposition rates to yield a conformal shell reveals a thin oxide layer on the Si\{113\} facet. This observation and control experiments suggest that facet-selective growth is enabled by the formation of an oxide, which prevents subsequent shell growth on the Si\{113\} NW facets. Further studies of facet-selective epitaxial growth of CdS shells on micro-to-mesoscale wires, which allows tuning of the lateral width of the compound semiconductor layer without lithographic patterning, and InP shell growth on Si NWs demonstrate the generality of our growth technique. In addition, photoluminescence imaging and spectroscopy show that the epitaxial shells display strong and clean band edge emission, confirming their high photonic
quality, and thus suggesting that facet-selective epitaxy on NW substrates represents a promising route to integration of compound semiconductors on Si.

2.1 Introduction

Integration of Si and compound III–V or II–VI semiconductors is an attractive goal since such heterostructures could marry the attractive photonic properties of direct band gap compound semiconductors with Si devices (1). However, mismatches in lattice constant, thermal expansion coefficient, and polarity between Si and compound semiconductors render growth of epitaxial heterostructures challenging (2,3). Nanowires (NWs) represent a promising platform for the integration of Si and compound semiconductors since their small cross-sectional footprint and surface area can alleviate issues created by lattice, thermal, and polarity mismatches (4,5). Thus far, several general strategies have been explored for compound semiconductor integration with Si in NWs. First, nanoparticle-catalyzed growth has yielded a variety of axially modulated group IV/III–V and II–VI NW heterostructures (6-10). Second, III–V and II–VI NWs have been grown vertically on Si and germanium substrates (11-27) and on Si NWs, forming branched heterostructure NWs (28). Lastly, there has been recent interest in core/shell heterostructure NWs, though the Si/III–V or II–VI core/shell interfaces are often difficult to control (29) or have not been characterized (30) and shells of high crystal quality with thicknesses beyond several nanometers have not been explored (6,31,32).

Conceptually, facet-selective growth provides a means by which to reduce the interfacial area of mismatched materials since the growing layer is confined to the width of the facet on which it is deposited. We previously reported the synthesis of crystalline core/shell Si NWs, which grow in the <211> direction and whose surfaces are terminated by well-defined Si{111},
{113}, and {110} facets (33). Studies have shown differences in growth rates of Si and Ge on the distinct Si surface facets, including (a) preferential Si growth on {113} facets in the presence of PH$_3$ (34) and (b) controlled growth of Ge on Si{111} and {110} surfaces (35). Here, we investigate the growth of CdS and InP shells, which are prototypical II–VI and III–V compounds, on Si NWs with well-defined facets, as shown schematically in Figure 2.1A.

2.2 Results and Discussion

Si NWs with well-developed facets and diameters from 200 to 400 nm (Figure 2.1B, top) were grown according to a previously described (33) procedure (Appendix 1). The growth substrate with the faceted Si NWs was dipped in aqueous buffered hydrofluoric acid (BHF) for 20 s to remove surface oxide, rinsed for 5 s in deionized water, and then submerged in liquid nitrogen to prevent collapse of the NWs via capillary forces during liquid water evaporation (33). The frozen growth substrate was quickly transferred to the second zone of a 3-zone furnace, and the tube was evacuated to a base pressure of 50 mTorr; during this process, the ice sublimed. Once at base pressure, the furnace was purged three times each with Ar and H$_2$, and the pressure was set at ~2.8 Torr with a flow rate of 20 standard cubic centimeters per minute (sccm) H$_2$. CdS was evaporated at 670–710 °C from zone 1 and deposited on the substrate in zone 2 at 450–550 °C for 5–40 min.
Figure 2.1 Facet-selective epitaxy on Si NWs. (A) Schematic depicting facet-selective growth of a shell material (orange) on faceted Si NWs (cyan). (B) Top, SEM image of a faceted Si NW before CdS growth. Bottom, SEM image of a Si/CdS heterostructure NW following CdS deposition. The blue and red arrows indicate CdS on Si{111} and {110} facets (33), respectively. Scale bars, 500 nm. (C) STEM EDS elemental mapping of Si (blue), Cd (red), and S (green) of a NW oriented in the Si <110> zone axis. Scale bar, 500 nm.

Scanning electron microscope (SEM) images of the Si NWs before and following CdS growth reveal several key features (Figure 2.1B). First, before growth, the Si NWs exhibit well-faceted structures similar to our previous report (33). Second, following CdS growth, the SEM
image shows CdS on distinct facets of the Si NWs. Specifically, the image shows that (i) the CdS forms a continuous stripe along the upper/lower facets and islands along the much narrower middle facet and that (ii) the intervening facets are free of deposited CdS. Comparison of the Si NW image to previous work (33) suggests that the continuous CdS growth occurs on Si NW \{111\} facets, while the islands form on \{110\} facets. Indeed, elemental mapping via energy-dispersive X-ray spectroscopy (EDS) in a scanning transmission electron microscope (STEM; Figure 2.1C) shows the spatial distributions of Si (blue), Cd (red), and S (green) from a Si NW oriented in the Si <110> zone axis. The elemental distribution matches the geometry shown in the schematic and the SEM images of Figure 2.1A,B, and moreover confirms that the CdS shells are primarily localized on the Si\{111\} facets. Additionally, SEM images indicate that the yield of facet-selective NWs is >95% (Appendix 2).

To further characterize the facet-selective Si/CdS NW structure, we used plan-view aberration-corrected TEM (Figure 2.2). As depicted schematically in Figure 2.2A, plan-view TEM of facet-selective Si/CdS NWs oriented in the Si[111] zone axis allows for inspection of the Si-CdS\{111\} interface in plan-view and the Si-CdS\{110\} interface in cross-section. The TEM image of the Si-CdS\{111\} interface in plan-view (Figure 2.2B) shows a high contrast area on the left, due to CdS on the Si, while the lower contrast area on the right corresponds to exposed Si. The clear boundary between the Si and CdS in Figure 2.2B confirms that, in agreement with Figure 2.1, CdS deposits selectively on the Si\{111\} surface facets of the Si NW and does not extend onto the Si\{113\} surface. In addition, a fast Fourier transform (FFT) of the exposed Si region (Figure 2.2C, II) yields a hexagonal pattern that can be indexed to Si \langle111\rangle and is consistent with the imaging zone axis and facet orientation. The FFT of the CdS/Si region is a convolution of spots from two layers of CdS and the Si NW (Figure 2.2C, I), as expected
from the imaging geometry. Importantly, it is possible to index the distinct CdS hexagonal spots to wurtzite CdS $<0001>$ due to the presence of $\{1100\}$ reflections in the FFT, which would not be present in a FFT of zinc-blende CdS. The orientations of Si and CdS spots with identical symmetries in the FFTs are equivalent, strongly suggesting that the orientation of the CdS is determined by epitaxy with the underlying Si$\{111\}$ surface.

**Figure 2.2** Plan-view TEM imaging of facet-selective Si/CdS heterostructure NWs. (A) Side- and top-view schematics of plan-view TEM imaging of facet-selective Si/CdS NWs oriented in the Si $<111>$ zone axis. (B) Plan-view TEM image of the Si-CdS$\{111\}$ interface showing the Si$\{113\}$ facet (right) and CdS grown on the Si$\{111\}$ facet (left). Scale bar, 4 nm. (C) FFTs from the CdS/Si and bare Si regions as depicted by (I) and (II) in (B), respectively. (D) Crystal
Figure 2.2, Continued: structure model oriented in the Si <111> zone axis showing CdS epitaxially grown on a Si{111} facet next to a bare Si{113} facet. Crystal directions are indicated on the right. (E) Plan-view TEM image of the Si-CdS{110} interface showing the Si{113} facet (left) and CdS grown on the Si{110} facet (right). Scale bar, 4 nm. Inset, FFT from the CdS in the TEM image. (F) Side- and top-view schematics of plan-view TEM imaging of facet-selective Si/CdS NWs oriented in the Si <113> zone axis. (G) TEM image of a facet-selective Si/CdS NW in the Si <113> zone axis. Scale bar, 4 nm. Inset, FFT from the Si in the TEM image.

A crystal structure model based on the TEM image and FFT analyses of the Si <111>/CdS <0001> zone axis (Figure 2.2D) depicts wurtzite phase CdS (left: sulfur, purple; Cd, yellow) growing epitaxially on a Si{111} surface adjacent to an exposed Si{113} facet (right, blue). As in their corresponding FFTs, both Si{111} and CdS{0001} have hexagonal symmetry, highlighted by the dashed hexagon in the model. Since the Si NW crystal structure is cubic whereas the CdS displays hexagonal (wurtzite) crystal symmetry, we note that, to our knowledge, this work presents the first report of clearly characterized heteroepitaxial polytypism, which is localized to specific facets of a NW.

Additional plan-view TEM imaging of the Si-CdS interface at the Si{110} facet (Figure 2.2E and schematic Figure 2.2A) shows that lattice fringes extend continuously from Si to the CdS, and moreover, there is no evidence for an interfacial layer. The FFT from this image (Figure 2.2E, inset) was indexed to CdS <1211>, which indicates that the CdS <1010> and Si <110> directions are parallel. Moreover, CdS lattice fringes, with 0.37 nm spacing, are in agreement with CdS{1010} planes parallel to the Si{110} facet. Together, these observations confirm that CdS growth on the Si{110} facets was also epitaxial. We also tilted facet-selective
Si/CdS NWs into the Si <113> zone axis (schematic, Figure 2.2F) to allow for plan-view imaging of the Si\{113\} facets. Figure 2.2G shows a TEM image of a Si\{113\} facet, where high contrast CdS grown on the adjacent Si\{111\} facet is observed on the left and the low contrast Si\{113\} facet is seen on the right. An FFT (Figure 2.2G, inset) from the Si region confirms the zone axis as Si <113>. TEM imaging in the Si <113> zone axis does not yield any detectable CdS on the Si\{113\} facets.

We observe facet-selective CdS growth on Si NWs along the majority of the growth substrate. However, Si NWs closest to the upstream CdS source where the Cd/S reactant concentration is highest (36) (Figure 2.3A) show conformal CdS shells on the Si NW cores. To better probe the mechanism of facet-selective growth, we characterized the conformal core/shell Si/CdS NWs with cross-sectional TEM imaging (Appendix 1). A low magnification TEM view and schematic of the cross-section (Figure 2.3A, top and bottom) show the low contrast Si NW core with smooth surface facets, the concentric high contrast CdS shell, and an amorphous sacrificial carbon layer, which was deposited for sample preparation. The notch in the bottom right of the cross-section was caused by Ga FIB damage during cross-section thinning. The conformal Si/CdS NW displays smooth CdS surfaces parallel to the Si\{111\} facets but rough CdS surfaces parallel to the Si\{113\} facets, as shown schematically in the bottom of Figure 2.3A.

In addition, higher resolution TEM images of the Si-CdS\{111\} interface (Figure 2.3B) show continuous lattice fringes from the Si to the CdS and no interfacial layer between the Si NW and CdS. We index FFTs of the Si (Figure 2.3D, I) and CdS (Figure 2.3D, II) to Si <211> and CdS <2110>, respectively. Both FFTs and their respective crystal directions have identical symmetry. The Si[211] crystal direction matches the previously reported growth direction of our
Si NWs (33). Moreover, the periodically spaced 0.67 nm CdS lattice fringes parallel to the Si-CdS{111} interface show that the CdS growth direction normal to the Si{111} facet is <0001>. Fourier-filtered TEM images of the Si-CdS{111} interface (Appendix 3) show misfit dislocations ~4 nm from the interface. Additionally, TEM images of the CdS recorded greater than ~30 nm from the Si-CdS {111} interface (Appendix 3) reveal that the CdS is practically free of defects. We note that no evidence for antiphase boundaries in the CdS layer (37) were observed in our TEM imaging studies; however, we acknowledge that this does not eliminate the possibility of such defects, particularly along a given CdS on Si{111} facet. Taken together, this evidence confirms the epitaxial relationship between the Si and CdS on the Si{111} interface, consistent with the plan-view TEM analysis of the facet-selective Si/CdS NWs in Figure 2.2.

Interestingly, TEM images of the Si-CdS{113} interface (Figure 2.3C) reveal a ~3 nm layer, which interrupts the Si (left) and CdS (right) lattice fringes and which is devoid of structural features and fringes. An FFT recorded from the CdS (Figure 2.3D, III) reveals randomly angled spot patterns, indicating that the CdS in this region is polycrystalline, in agreement with the rough CdS shell surface observed parallel to the Si{113} surfaces (36). Together, this evidence indicates that the interfacial layer is amorphous. An aberration-corrected STEM EDS line scan (Figure 2.3E) reveals the presence of oxygen, consistent with amorphous silicon oxide in the interfacial layer separating Si and CdS.

Based on the above data, we propose that facet-selective growth of CdS on the Si{111} and {110} facets can be attributed at least in part to a passivating amorphous silicon oxide layer on the Si{113} facets. Although oxide is removed from the Si NWs immediately prior to placement in the CdS growth reactor, previous literature has reported that the sticking coefficient of water is 2 orders of magnitude higher for Si{113} than for Si{111} (38,39) and that adsorbed
water decomposes to form silicon surface oxide at temperatures comparable to our CdS growth (40,41). The continuous lattice fringes observed at the \{111\} interface (Figure 2.3B) suggest that oxygen-containing impurities are not significantly incorporated into this interface. However, given the base pressure of our growth apparatus, it is possible that residual water/oxygen can lead to oxide formation on Si\{113\} prior to deposition of CdS. Since there is no chemical difference between the Si NWs upstream and downstream (relative to the CdS reactant source), the Si\{113\} oxide forms on NWs in both positions. However, the difference in CdS flux between upstream and downstream locations results in facet-selectivity. Upstream, CdS shells grow conformally because the higher reactant flux precludes sufficient time for diffusion and/or desorption. This suggestion is consistent with the ~1−2 µm CdS shells on upstream Si NWs (Figure 2.3A). In contrast, the lower CdS flux at the downstream position (36) allows for diffusion and/or desorption from the \{113\} oxide before incorporation into the shell, thereby yielding facet-selective CdS growth.
Figure 2.3 Cross-sectional TEM imaging of a conformal Si/CdS core/shell NW. (A) Top, TEM image of a cross-section from the conformal core/shell Si/CdS NW. Scale bar, 200 nm. Bottom, schematic depicting the geometry of the cross-section. B and C denote areas where the Si-CdS{111} and {113} interfaces are imaged at high magnification and presented in (B) and (C); I, II, and III refer to the FFT locations in (D). (B,C) Aberration-corrected TEM images of the Si-CdS (B) {111} and (C) {113} interfaces. Scale bars, 2 nm. Red dashed lines denote (B) the interface between Si and CdS and (C) an interfacial layer between the Si and CdS. (D) FFTs derived from ~35 x 35 nm2 areas of (I) Si, (II) CdS grown on the Si{111} facet, and (III) CdS grown on the Si{113} facet. (E) STEM EDS line scan profile of Si (blue), O (orange), Cd (red), and S (green) through the Si-CdS{113} interface. The elemental intensity profiles are overlaid on a STEM image of the interface. The white line is ~17 nm long.

To better understand the role of oxide in the growth of CdS on Si NWs, we grew CdS on faceted Si NWs without removal of the Si NW native surface oxide prior to CdS deposition (Appendix 4). In the upstream position, SEM images show conformal CdS shells with rough
surfaces that are consistent with deposition of a fully polycrystalline shell. This contrasts with the well-developed \{0001\} facets observed when the native surface oxide was removed immediately prior to growth (Figure 2.3A). In the downstream position, SEM images show that no continuous CdS shell forms on any facets of the Si NWs with native oxide, in contrast to the facet-selective growth under the same conditions when the oxide was removed prior to growth (Figure 2.1B).

We note an analogy between our proposed mechanism and selective area epitaxy/growth (SAE/SAG), which have been implemented to epitaxially grow group IV, II–VI, or III–V films (42-47) and NWs (23-27) on lattice-mismatched substrates. In SAE, an amorphous oxide or nitride mask layer is deposited on a substrate and holes or trenches are patterned in the mask layer. Precursor flux is controlled such that long adatom diffusion lengths result in selective film growth on the exposed substrate rather than on the mask. However, we note that the novelty of facet-selective epitaxy on NW substrates stems from (1) intrinsic “patterning” of the substrate with faceted NW structures and (2) the natural formation of an oxide due to the difference in facet reactivity without the need for any lithographic patterning.

Therefore, our facet-selective epitaxy approach should be general for 1D Si structures and likely other NWs as well. To first evaluate this generality we deposited CdS on micrometer diameter Si wires (Figure 2.4A,B). SEM images of the resultant heterostructures reveal facet-selective growth of CdS on the Si\{111\} facets. Second, we demonstrate the generality toward other shell materials by growing indium phosphide (InP) on faceted Si NWs. SEM imaging of InP growth carried out in a manner similar to the deposition of CdS (Appendix 1) on Si NWs (Figure 2.4C) confirms that InP islands grow selectively on the Si\{111\} facets and that the Si\{113\} facets remain free of InP.
Figure 2.4 Generality of facet-selective epitaxy. (A,B) Facet-selective CdS growth on Si wires of various sizes. SEM image of Si/CdS heterostructure wires with diameters of ca. (A) 3 and (B) 10 μm. Scale bars, 2 μm. (C) Left, SEM image of a Si/InP heterostructure NW. Scale bar, 400 nm. Right, schematic depicting the crystallography of the facet-selective Si/InP structure.

Finally, we characterized the optical properties of the facet-selective Si/CdS heterostructure NWs. A scanning confocal photoluminescence image of facet-selective Si/CdS heterostructure NWs randomly dispersed on a quartz substrate (Figure 2.5A) reveals strong green emission. Comparison of NW positions determined by bright-field and photoluminescence images demonstrates that every NW in the field of view exhibits strong luminescence. Moreover, a representative room temperature photoluminescence spectrum from a single Si/CdS NW (Figure 2.5B) shows a symmetric emission profile, featuring strong band-edge emission at ~514 nm (2.4 eV), which is consistent with high quality crystalline bulk CdS. We do not observe any strong emission except for the band-edge peak, indicating that the CdS on the faceted Si NWs has a relatively low concentration of S-vacancy defects (48), does not display optical
characteristics indicative of quantum confinement (49), and is of high optical quality. Therefore, facet-selective Si/CdS NWs show potential for integration of compound semiconductors with Si for (opto)electronics.

**Figure 2.5** Optical characterization of the facet-selective Si/CdS heterostructure NWs. (A) Scanning confocal photoluminescence image of facet-selective Si/CdS heterostructure NWs randomly dispersed on a quartz substrate. (B) Room temperature photoluminescence spectrum from a single Si/CdS NW. The green arrow indicates the wavelength of band-edge (514 nm; 2.4 eV) emission from high quality crystalline bulk CdS; the red arrow indicates the previously reported wavelength of emission due to S-vacancy defects (~730 nm; 1.7 eV) (48).
2.3 Conclusions

In summary, we have demonstrated facet-selective growth of CdS on Si NWs. Aberration-corrected transmission electron microscopy analyses have shown that the crystalline CdS is grown epitaxially on the \{111\} and \{110\} surface facets of the Si NWs and that the Si\{113\} facets remain bare. Further analysis of conformal CdS shells on Si NWs grown at higher deposition rates revealed a thin oxide layer on the Si\{113\} facet, suggesting that the facet-selective growth is enabled by the formation of an oxide, which prevents subsequent shell growth on the Si\{113\} NW facets. Further studies of the generality of facet-selective epitaxial growth demonstrated the potential of the technique on micro-to-mesoscale wires, which allows tuning of the lateral width of the compound semiconductor layer without lithographic patterning and InP shell growth on Si NWs. In addition, photoluminescence imaging and spectroscopy show that the epitaxial shells display strong and clean band edge emission, thus confirming their high photonic quality, suggesting that facet selective epitaxy on 1D Si structures could serve as a unique platform for integrating compound semiconductors with group IV materials in (opto)electronics.

2.4 References

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Chapter 3: Plateau-Rayleigh crystal growth of periodic shells on one-dimensional substrates

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The Plateau-Rayleigh instability was first proposed in the mid-1800s to describe how a column of water breaks apart into droplets to lower its surface tension. This instability was later generalized to account for the constant volume rearrangement of various one-dimensional liquid and solid materials. Here, we report a growth phenomenon that is unique to one-dimensional materials and exploits the underlying physics of the Plateau-Rayleigh instability. We term the phenomenon Plateau-Rayleigh crystal growth and demonstrate that it can be used to grow periodic shells on one-dimensional substrates. Specifically, we show that for certain conditions, depositing Si onto uniform-diameter Si cores, Ge onto Ge cores and Ge onto Si cores can generate diameter-modulated core–shell nanowires (NWs). Rational control of deposition conditions enables tuning of distinct morphological features, including diameter-modulation periodicity and amplitude and cross-sectional anisotropy. Our results suggest that surface energy reductions drive the formation of periodic shells, and that variation in kinetic terms and crystal facet energetics provide the means for tunability.

3.1 Introduction

Controlling crystal growth at the nanoscale allows for command over both morphology and composition, thereby imparting enhanced or new functionality (Chapter 1). For example, radial growth of conformal, crystalline shells over NW cores (1-4) provides a way to introduce unique electronic and optical characteristics to uniform-diameter core–shell nanomaterials (5-7).
Key physical phenomena, including optical absorption and electrical and thermal transport, are influenced by a NW's diameter (5,8, Chapter 1), so it is interesting to consider whether diameter modulation can be introduced synthetically by design to generate material properties distinct from those of uniform-diameter NWs. Several reports have been published on diameter-modulated NWs synthesized by perturbing NW growth during axial elongation (9-16), by post-growth ex situ methods (17,18) and by strain-mediated core–shell heterostructure growth (19,20). However, the ability of these techniques to simultaneously control multiple morphological features, tune these features over a wide range and combine cores and shells of arbitrary material composition remains limited.

Here, we report a general method of synthesizing diameter-modulated core–shell NWs whose morphologies are tunable over an unprecedented range. We term this process ‘Plateau-Rayleigh crystal growth’, as it can be understood by considering the physics underlying the Plateau-Rayleigh (P-R) instability but in the context of NW crystalline shell growth. The P-R instability (21-26), first proposed in the 1800s to explain the break-up of a column of water into isolated droplets, more generally describes the constant-volume transformations of one-dimensional liquids and solids that reduce the total surface tension or energy. The relationships between in situ periodic shell growth by P-R crystal growth on a one-dimensional NW core versus conventional conformal shell growth and the P-R instability are shown schematically in Figure 3.1A. Without a reactant, annealing NWs at low pressures yields isolated nanocrystals (27-29), with a periodic spacing predetermined by the NW diameter due to the P-R instability. Here, by introducing reactant at low pressures, we reveal an unexplored growth regime, P-R crystal growth, where the diameter-modulation periodicity (pitch) and diameter-modulation amplitude (inner and outer diameters) are controlled for a given NW diameter.
Figure 3.1 Plateau-Rayleigh (P-R) crystal growth of periodic shell NWs with tunable morphology. (A) Schematic illustrating P-R instability, conformal shell growth and P-R crystal
Figure 3.1, Continued: growth of periodic shells on NW cores at elevated temperatures. Pitch is defined as the sum of lengths of an inner and outer shell. (B) SEM image of Si particles obtained after annealing 100 nm Si NW cores in vacuum at 900 °C for 3 min. Scale bar, 2 μm. (C) Plan-view SEM images showing tunability of pitch from 2 to 12 μm for Si shells deposited on 100 nm Si NW cores. Growth conditions (temperature (°C), SiH₄ flow (sccm), H₂ flow (sccm), total pressure (Torr), SiH₄ partial pressure (mTorr)) for images (top to bottom) were (775/0.3/180/0.61/1), (760/0.15/60/0.29/0.7), (800/0.8/60/0.29/4) and (775/1/60/0.29/5), respectively. Scale bars, 1 μm. (D) Crystallographic characterization of Si periodic shell NWs. Top, composite bright-field TEM image of a Si periodic shell NW with average pitch of ~2.2 μm. The image consists of four individual low-magnification images stitched together. Image borders are indicated by dashed blue lines. Scale bar, 1 μm. Bottom left and middle, bright- and dark-field TEM images from the area indicated by the red arrow. Scale bars, 400 nm. The dark-field TEM image was recorded using a {220} reflected beam. Inset, schematic depicting the cross-sectional geometry and surface facet assignments of the periodic shell NWs. Bottom right, selected area electron diffraction patterns in the [111] zone axis from the region shown in the left and middle panels.

3.2 Results and Discussion

We focus on Si periodic shell growth (see Appendix 5), because previous work has reported conformal Si shell growth over 100-nm-diameter Si cores under a wide range of experimental conditions (4,7), including temperatures between 650 and 850 °C with silane (SiH₄) as the Si shell source. In the absence of SiH₄, heating 100-nm-diameter Si NWs at temperatures ≥775 °C leads to break-up into nanoparticles due to the P-R instability. At 900 °C this transformation occurs within 3 min (Figure 3.1B), and much more slowly at lower temperatures (for example, >14 h at 775 °C), as expected (27-29). Scanning electron microscopy (SEM) images (Figure 3.1C) of NWs produced following growth in the same temperature range (650–850 °C) but with SiH₄ and H₂ partial pressures ~10–100 times lower than for conventional
conformal shell growth (see Appendix 5) highlight new features. First, the images show a periodic diameter modulation, where the pitch of the modulation varies as a function of specific growth conditions. Specifically, the periodic shell growth temperatures (in °C), SiH$_4$ flow rates (in sccm) and partial pressures (in mTorr) for these images (top to bottom) were 775/0.3/1, 760/0.15/0.7, 800/0.8/4 and 775/1/5, respectively (Figure 3.1C). Second, the periodic structure results from an additive process, because the inner/outer diameters of the modulations shown in the four images are all greater than the ~100 nm starting NW core diameter (280/490, 160/270, 170/320 and 180/330 nm). Furthermore, annealing 100 nm Si cores for ~2 h at a temperature similar to these growths (Appendix 6) does not lead to any significant structural rearrangement of the core on the timescale relevant to periodic shell formation. Hence, these results show that the periodic shell structures arise from added SiH$_4$ as predicted by our P-R crystal growth concept. In addition, the yield of diameter-modulated NW structures is quite high, ~80–90%, as determined from optical and SEM images (Appendix 7). Finally, control experiments in which the nanoparticle catalyst was removed by etching before shell growth (Appendix 8) showed similar periodic structures and highlight that the observed modulation does not arise from diffusion of the metal catalyst along the NW core.

The structure and composition of these periodic shell NWs have been characterized by transmission electron microscopy (TEM; see Appendix 5). A representative low-magnification TEM image (Figure 3.1D) depicts a periodic shell NW with pitch of ~2 μm. Inspection of the interface between inner and outer shells by bright-field and dark-field imaging fails to indicate any defects observable in the [111] (Figure 3.1D, left and middle) and [110] (Appendix 9) zone axes. Selected-area electron diffraction data obtained from different positions along the NW axis, including the inner and outer diameters of the modulation and interface between an inner/outer
modulation, produced indistinguishable diffraction patterns; that is, the diffraction patterns all have a single set of spots in the [111] zone axis (Figure 3.1D, right), indicating a [211] NW growth axis consistent with epitaxial, diameter-modulated growth and our previous work (4). Elemental mapping by energy-dispersive X-ray spectroscopy (EDS; Appendix 10) also confirmed that added material was Si, without appreciable impurities, showing that the NW composition is uniform along its axis within the 0.1–1% sensitivity of EDS. Together, TEM imaging, diffraction and compositional analyses demonstrate that the Si periodic shell NWs are highly crystalline materials with clean core/shell interfaces and axial uniformity with respect to crystallography and composition.

To illuminate factors controlling the P-R crystal growth of periodic shells we explored growths where only time, SiH$_4$ flow rate or temperature was systematically changed. SEM images of periodic shell structures produced by varying the growth time from 0 to 8 min at 800 °C (SiH$_4$ flow = 0.8 sccm; SiH$_4$ partial pressure = 4 mTorr; Appendix 11) show the development of a diameter-modulated shell from a 100-nm-diameter Si NW. Analysis shows that the pitch, ~4.5 μm, does not change with time, although the diameters of the inner and outer shells increase as expected for this additive process. The diameter-modulation amplitude and outer shell fill ratio, which is defined as the ratio of outer shell length to the pitch, do change with time. Studies carried out with different SiH$_4$ flow rates at 775 °C and with other parameters constant (Figure 3.2A and Appendix 12) yielded systematic increases in average pitch: 1.2 ± 0.18, 2.5 ± 0.32, 3.8 ± 0.85 and 7.8 ± 1.42 μm (±1 standard deviation (s.d.), N = 10 for all measurements) for flow rates/SiH$_4$ partial pressures of 9/47, 3/15, 1/5 and 0.3/1 sccm/mTorr, respectively. Growths carried out at different temperatures with the SiH$_4$ flow rate and partial pressure (3 sccm/15 mTorr) and other parameters constant (Figure 3.2B and Appendix 13).
produced average pitches of $1.2 \pm 0.16$, $2.5 \pm 0.32$, $4.0 \pm 0.84$ and $8.3 \pm 0.87$ μm ($\pm 1$ s.d., $N = 10$ for all measurements) at growth temperatures of $735$, $775$, $815$ and $855$ °C, respectively. These studies show that the pitch can be systematically increased by increasing the temperature or decreasing the SiH$_4$ flow rate/partial pressure during growth.
Figure 3.2 Experimental synthetic control and model for P-R crystal growth. (A) Dependence of pitch on \( \text{SiH}_4 \) flow rate/partial pressure. Si shells were deposited on 100 nm Si cores at 775 °C for variable \( \text{SiH}_4 \) flow rates (partial pressures) at a total pressure of ~0.3 Torr. Error bars denote
Figure 3.2, Continued: 1 s.d. from an average of ten NW measurements. SEM images of NWs grown at variable SiH$_4$ flow rates are shown in Appendix 12. (B) Dependence of pitch on temperature. Si shells were deposited on 100 nm Si cores at variable temperature with a SiH$_4$ flow rate of 3 sccm (SiH$_4$ partial pressure of 15 mTorr) at a total pressure of ~0.3 Torr. Error bars denote 1 s.d. from an average of ten NW measurements. SEM images of NWs grown at variable temperatures are shown in Appendix 13. (C) Surface area comparisons for variable pitch. The surface areas of periodic shell NWs with various pitches are compared to a uniform-diameter (straight) NW with equivalent volume, as denoted by the dashed grey line. All structures have equivalent volume and the lowest possible surface-area configuration for a given pitch. Right axis, absolute output values from the calculations assuming a total NW length of 30 $\mu$m, inner diameter of 100 nm and the pitch denoted on the bottom axis. Left axis, dimensionless ratio of the surface area of a periodic shell NW to the surface area of a uniform-diameter core–shell NW of equivalent volume.

To rationalize these experimental observations and explore the potential for synthetic design of new periodic structures, we considered a simple model for P-R crystal growth. Similar to P-R instability, where periodically spaced particles reduce the total surface energy compared to the original one-dimensional material, we assume that periodically spaced shells on a one-dimensional substrate reduce the total surface energy compared to a uniform-diameter NW of equivalent volume, thermodynamically driving growth of periodic shells over uniform-diameter shells. Moreover, we assume that longer-pitch NWs have lower surface energies than shorter-pitch NWs of equivalent volume. The kinetics of the growth, however, will determine (1) whether periodic (versus uniform-diameter) shells grow and (2) whether longer, lower-energy pitches develop. In the periodic shell growth regime (735–855 °C, ~0.1 Torr), the diffusion length of adatoms is known to play a significant role in determining the final morphology and structure of Si films (30, 31; Appendix 5). Thus, we hypothesize that Si adatom diffusion lengths
are the most significant kinetic factor allowing access to lower-energy (that is, longer-pitch) periodic shell structures.

Our experimental results support the above model and highlight the implicit influence of kinetics for achieving lower-energy periodic configurations. First, Figure 3.2A,B shows that lower SiH$_4$ flow rates/partial pressures and higher temperatures yield longer pitches, and corresponding thin-film studies have shown that lower precursor fluxes and higher temperatures are correlated with longer surface diffusion lengths (30). Second, increasing only the H$_2$ partial pressure 100-fold but with a growth temperature and SiH$_4$ partial pressure that would otherwise produce periodic shells yields conformal shells. This result is consistent with the fact that surface diffusion lengths of Si adatoms are reduced by H$_2$ pressure (27); that is, growth is kinetically trapped to yield higher-surface-energy conformal shells. Third, the introduction of PH$_3$ impurity leads to a reduction in periodic shell pitch from ~2.5 to 1.5 $\mu$m and ultimately conformal shells at higher PH$_3$ levels (Appendix 14), consistent with decreased adatom surface diffusion lengths during Si film growth in the presence of PH$_3$ (32). Finally, estimated diffusion lengths in the periodic shell growth regime range from 200 nm at lower temperatures to tens of micrometers at our highest growth temperatures (Appendix 5) are consistent with the observed periodic shell pitch values.

Our model assumes that periodically spaced shells on a NW can have reduced surface energies compared to uniform-diameter core–shell NWs of the same volume by reducing the total surface area and/or by elaboration of lower-energy surface facets. A straightforward geometric analysis (Appendix 5) allows us to test this assumption by directly comparing the ratio of surface areas for different periodic versus conformal shell configurations, given the general correspondence of surface area and surface energy (30, 33). For example, a periodic shell NW
with a pitch of 3 μm, outer shell diameter of ~400 nm and inner shell of ~100 nm can have 92% of the surface area of a uniform-diameter NW with equivalent volume (Appendix 15). Similar calculations show that surface area decreases with increasing pitch as more of the Si volume becomes concentrated into fewer shells (Figure 3.2C and Appendix 15). This latter trend is consistent with the experimental results described above, where conditions that increase the adatom diffusion length lead to longer pitch structures. We note that our model and geometric analysis are general, as they assume a cylindrical cross-section and isotropic surface energy densities.

We have also carried out calculations that explicitly consider the experimentally observed cross-sections and the corresponding energy densities for the different Si surface facets observed on our Si periodic shell structures (Appendices 5 and 15). Notably, these calculations show that our observed periodic shell NWs have lower surface energies than uniform-diameter NWs with equivalent volumes. Thus, the concepts and predictive trends of the model should be applicable to other material systems, sizes and cross-sectional geometries.

We explored the generality of P-R crystal growth through Si shell growth on different-diameter Si NW cores and the growth of other materials. SEM images of periodic Si shell structures from growth on Si NW cores with diameters of 50, 30 and 20 nm (Figure 3.3A-C, respectively) highlight several points. First, these images demonstrate that P-R crystal growth yields periodic shell NWs for a broad range of ‘substrate’ NW diameters. Second, these data show that pitches of periodic shells grown on smaller 30- and 20-nm-diameter NWs can easily reach sub-micrometer dimensions with values of ~600 and ~330 nm, respectively. Third, these results demonstrate that periodic shell growth can yield substantial width-to-height anisotropy (addressed in more detail in the following). In addition, high-resolution, lattice-resolved TEM
data obtained at the junction between one inner core and outer shell from a Si periodic shell
grown on a 20-nm-diameter Si NW core (Figure 3.3D) show continuous lattice fringes over the
entire structure with no indications of defects or an interface between the core and shell. Selected
area electron diffraction from this region (Figure 3.3D, inset) yielded a single set of spots in the
[111] zone axis. We note that the diffraction pattern and principle crystal directions of the NW
core and shell are the same as those found for the larger low-aspect-ratio periodic shell structures
obtained from P-R crystal growth on 100 nm Si NWs (for example, Figure 3.1D).
Figure 3.3 Generality and scope of P-R crystal growth. (A-D) Generality with respect to core diameter. SEM images of Si periodic shells deposited on Si NW cores with diameters of (A) 50
Figure 3.3, Continued: nm, (B) 30 nm, and (C) 20 nm. Scale bars, 400 nm. Si shells in (A) were deposited at 815 °C for 10 min with SiH₄ and H₂ flow rates of 0.3 sccm and 60 sccm, respectively (SiH₄ partial pressure, 1 mTorr). In (B) and (C), Si shells were deposited at 775 °C for 3 min with SiH₄ and H₂ flow rates of 3 sccm and 200 sccm, respectively (SiH₄ partial pressure, 10 mTorr). (D) High-resolution TEM image of the transition from inner to outer shell of a Si periodic shell grown on a 20 nm core NW. Scale bar, 10 nm. Inset, selected area electron diffraction pattern in the [111] zone axis of the region of the NW shown in the TEM image. (E-G) Synthetic control of aspect ratio. Head-on SEM images of (E) low (∼1) and (F) high (∼4) aspect ratio Si periodic shells grown on 100 nm Si NW cores. At 735 °C with a H₂ flow rate of 60 sccm, Si shells were deposited using SiH₄ flow rates/partial pressures of 3 sccm/15 mTorr for (E) 5 min and (F) 0.3 sccm/1 mTorr for 22 min. Scale bars, 400 nm. (G) TEM image of the transition from inner to outer shell of a high (∼4) aspect ratio Si periodic shell grown on a 100 nm core NW. Scale bar, 400 nm. Inset, selected area electron diffraction pattern in the [111] zone axis of the region of the NW shown in the TEM image. (H) Generality of P-R crystal growth with respect to material. SEM image of Ge periodic shells deposited on a Ge NW core with a diameter of 50 nm. Scale bar, 400 nm. Ge shells were deposited for 10 min at 470 °C followed by deposition for 3 min at 600 °C with GeH₄ flow rate/partial pressure of 40 sccm/20 mTorr.

These diameter-dependent growth studies highlight a unique characteristic of P-R crystal growth—the capability to achieve substantial width-to-height anisotropy during periodic shell growth (Figure 3.3A-C). We suggest that the inherent anisotropies in crystal facet surface energies (34) and adatom diffusion coefficients (31, 35–37) enable synthetic tunability of aspect ratio. SEM images of structures resulting from P-R crystal growth on 100 nm Si NW cores under different conditions (Figure 3.3E,F) show periodic shells with a fourfold variation in cross-sectional anisotropy, supporting this idea. TEM images and electron diffraction data (Figure 3.3G) further show that the 4:1 anisotropy shell has the same structural quality and crystal directions as observed for periodic shell NWs with 1:1 cross-sectional geometry.
(Figure 3.1D) and periodic shell growth on 20 nm cores. Previous thin-film studies have reported net adatom diffusion from Si(111) to the Si(113) facets, elongating the (111) surface (31, 37). This is consistent with our work, where the higher-aspect-ratio structures, which have longer (111) surfaces, are observed with lower SiH$_4$ partial pressures and presumably longer diffusion lengths (Appendix 16). Unlike pitch, the aspect ratio depends on the total growth time as well as temperature, preventing a more quantitative analysis at the moment. Future modeling that accounts for the differences in surface facet energies, anisotropic diffusion lengths and the ratio of the diffusion lengths to surface facet lengths should enable more controlled anisotropic periodic shell growth.

We also explored P-R crystal growth of Ge periodic shells on Ge cores. Deposition of Ge onto 50 nm Ge NW cores with GeH$_4$ partial pressures ~20 times lower than used for conformal Ge shell growth (1) yields periodic shell structures consistent with our model. An SEM image of a Ge periodic shell structure (Figure 3.3H) grown at a GeH$_4$ partial pressure of 20 mTorr exhibits a pitch of 610 nm and an aspect ratio of ~1.5. Although P-R crystal growth of Ge periodic shell structures is more challenging than for Si, the fact that periodic Ge shells are obtained for a range of conditions (for example, 500–600 °C) suggests that the general concepts of surface energy minimization coupled with suitably long diffusion lengths will be applicable to the homoepitaxial growth of periodic shells on a wide range of one-dimensional materials.

One example of how P-R crystal growth can impart enhanced functionality is evident from the optical properties of diameter-modulated versus uniform-diameter NWs (4, 7, 38). A dark-field optical microscopy image of a 6-µm-pitch periodic structure with 205 nm inner and 260 nm outer diameters (Figure 3.4A) shows a modulation in the color of the scattered light coincident with the shell diameter modulation. The regions of different diameter efficiently
scatter (and absorb) distinct wavelengths of light. In addition, a dark-field image of a much shorter ~450-nm-pitch periodic NW with 30 nm inner and 150 nm outer diameters (Figure 3.4B; structural parameters determined from an SEM image of the same NW) shows a single scattering color with the intensity maxima and modulation correlated with the outer diameter region and pitch, respectively.

**Figure 3.4** Optical properties of Si periodic shell NWs. (A,B) Dark-field optical images of periodic shell NWs with different dimensions. The dimensions, determined from SEM measurements, are $D_{\text{outer}} = 260$ and 150 nm, $D_{\text{inner}} = 205$ and 30 nm and pitch = 6 $\mu$m and 450 nm in (A) and (B), respectively. Scale bars, (A) 10 $\mu$m and (B) 2 $\mu$m. (C,D) Light absorption of inner versus outer shell modeled by FDTD simulations. Inner diameters, outer diameters and pitches of the NWs in (A) and (B) were used as input dimensions for simulations in (C) and (D), respectively. Outer aspect ratios were assumed to be 1.45 and 1.5 ($H_{\text{outer}} = 180$ and 100 nm) and inner aspect ratios were 1.15 and 1.0 ($H_{\text{inner}} = 180$ and 30 nm) for (C) and (D), respectively. Spectra were obtained from finite-volume slices at the center of the outer (blue and red) and
Figure 3.4, Continued: inner (grey and green) shells (C, D). Insets, normalized absorption mode profiles at wavelengths of 445 nm (top) and 490 nm (bottom), denoted by 1 and 2 in (C), and at 590 nm, denoted by 3 in (D). Scale bars, (C) 250 nm and (D) 30 nm.

To understand these images and the potential for controlling optical properties with periodic shell structures, we carried out finite-difference time-domain (FDTD) simulations (see Appendix 5). First, simulations of the absorption spectra for the long-period NW (Figure 3.4C, dimensions from the NW in Figure 3.4A) highlight the distinct absorption properties of the inner (grey) and outer (blue) shells. The absorption peaks found at distinct wavelengths for the inner and outer segments, which give rise to the variation in color observed in the dark-field image in Figure 3.4A, correspond to resonant modes supported in these different-diameter regions. The optical resonant absorption mode profiles (Figure 3.4C, inset) at 445 nm (denoted 1) and 490 nm (denoted 2) illustrate the spatially distinct light absorption in the inner versus outer shell. Second, simulations carried out for the short-period NW show that resonant absorption peaks are only observed for the larger outer diameter portion of the periodic structure, with little or no mode intensity sustained in the ~30-nm-diameter inner region (Figure 3.4D, inset). Localized, spatially non-uniform axial absorption peaks are not observed for uniform-diameter Si NWs. We suggest that these periodic shell NWs structures could provide unique opportunities for optomechanical studies (39, 40). Specifically, their ability to sustain significant light confinement within the outer shells while having a reduced mass compared to uniform-diameter structures would be advantageous, as uniform-diameter NWs with equivalent mass would be unable to support such optical confinement. Reducing the mass for optomechanics allows for higher mass detection limits (40, 41) for resonator sensors and for
probing quantum-limited mechanical motion and coherently cooling or amplifying the mechanical motion of resonators (39).

Finally, FDTD simulations were used to explore short-period structures where the inner region is sufficiently large to sustain resonant absorption modes. Interestingly, with the inner/outer dimensions of the periodic shell NW in Figure 3.4A but with pitches <500 nm (Appendix 17), high-amplitude peaks emerge at wavelengths >700 nm that can be assigned as coupled grating modes (42). The calculated absorption efficiency for such a periodic shell NW is 0.7 at 929 nm, and bulk Si would require a thickness of ~50 μm to yield the same absorption efficiency. These results suggest that similar periodic shell NWs with enhanced and tunable near-infrared absorption could be exploited for photodetectors and other optoelectronic devices. Furthermore, although lithography can impose grating structures in two dimensions, a unique advantage of P-R crystal growth is the capability to realize fully three-dimensional gratings with tunable anisotropy and, moreover, to prepare periodic shells on the vertical NW arrays currently being explored for solar energy conversion (3) and structural color (43).

We have also explored the applicability of P-R crystal growth to the synthesis of core/periodic shell heterostructures. SEM images of a NW produced after introduction of GeH$_4$ at low pressures following the growth of 30-nm-diameter Si cores (Figure 3.5A-C) clearly shows the growth of Ge periodic shells on Si cores. Growths at a fixed temperature of 520 °C with GeH$_4$ flow rates/partial pressures of 40 sccm/16 mTorr (Figure 3.5A), 8 sccm/4 mTorr (Figure 3.5B) and 1 sccm/0.5 mTorr (Figure 3.5C) yielded periodic heterostructures with pitches of ~0.3, 0.9 and 2.4 μm, respectively. This observation of increasing pitch with decreasing reactant flow rate is consistent with the trend observed for Si periodic shell structures (Figure 3.2A) and our model. A complete understanding of the energetics of the heterostructure
growth will require consideration of other factors, including the relative energy densities of Si and Ge surfaces and the strain/interfacial energies (19,20). In fact, it is likely that interfacial strain energy terms help to drive the formation of periodic shells, which is supported by the absence of Ge growth on the Si core between the Ge periodic shells (in contrast with our homoepitaxial Si/Si or Ge/Ge periodic shell structures), as observed in SEM (Figure 3.5A-C) and TEM (Figure 3.5D) images. Higher-resolution TEM images (Figure 3.5D, right) and fast Fourier transform (FFT) analysis of the area suggest that the Ge shells are crystalline and grow epitaxially on the Si core, as indicated by the clear lattice fringes and two sets of related ‘diffraction’ spots in the FFT. To the best of our knowledge, our results are the first demonstration of pitch-controlled growth of radially conformal, Ge periodic shells on a Si core. The potential diversity of NW heterostructures combined with the empirical rules for P-R crystal growth demonstrated above suggest that periodic shell NW heterostructures represent a rich area for synthetic, physical measurement and theoretical exploration in the future.
Figure 3.5 P-R crystal growth of periodic shell heterostructures. (A-C) SEM images of Ge periodic shells on Si NW cores with diameters of 30 nm. Ge was deposited at 520 °C with H₂ flow rate of 60 sccm and GeH₄ flow rates/partial pressures of (A) 40 sccm/16 mTorr, (B) 8 sccm/4 mTorr and (C) 1 sccm/0.5 mTorr. Scale bars, 200 nm. (D) Left, TEM image of a Si/Ge core/periodic shell NW with average pitch of ~500 nm. Scale bar, 20 nm. Right, high-resolution TEM image of the area indicated by the white box. Scale bar, 5 nm. Inset, FFT from core–shell region.
3.3 Conclusions

In summary, we have presented a growth phenomenon that is fundamentally unique to one-dimensional materials: P-R crystal growth. Compared to previous reports of conformal shell growth, the deposition of shells at lower pressures and higher temperatures yields periodic shell structures for several core–shell material combinations, including Si on Si, Ge on Ge and Ge on Si, over a wide range of core diameters (20–100 nm). Tuning shell deposition conditions allows for a morphological control that is unprecedented compared to other synthetic methods with respect to both the range and number of controllable features (pitches from 400 nm to >12 μm, cross-sectional anisotropies from 1:1 to 4:1 and modulation amplitudes up to ~8:1). Our studies strongly suggest that periodic shell structures tend to minimize surface energy as long as lower-energy structures are kinetically accessible. The thermodynamic aspect of this model stems solely from a geometric consequence of adding volume to a one-dimensional structure and thus indicates a broad potential scope of P-R crystal growth, whereby periodic shells can reduce the surface area of a growing crystal irrespective of the size, material composition (for example, semiconductor, metal or dielectric) or origin of the one-dimensional substrate (vapor–liquid–solid (VLS) grown, top-down etched, and so on) and independent of the shell deposition process (chemical vapor deposition, solution-phase and similar). Thus, we expect our findings to have implications for material combinations and applications well beyond those mentioned here and, more generally, to illustrate the importance and opportunities in understanding the thermodynamics and kinetics unique to crystal growth on NWs and other low-dimensional systems.

3.4 References


Chapter 4: Shape-controlled deterministic assembly of nanowires

[The following chapter is derived in part from L. Xu et al. Submitted (2015).]

4.1 Introduction

Interest in the assembly of nanoscale wires has long been motivated by the development of bottom-up integrated nanodevice arrays and circuits (1-6). Existing assembly methods (7,8) can now be used to align (9-16) and in some cases deterministically position (17-20) straight nanoscale wires, but have not yet exploited the flexibility and large elastic strains sustainable in these nanoscale wires (21,22) for assembly of, for example, bent or curved nanoscale wires. Here, we demonstrate a new concept combining simultaneous assembly and “shaping” to achieve large-scale, high-precision shape controlled deterministic assembly of nanowires (NWs). We lithographically pattern shaped trenches and then shear transfer NWs to the patterned substrate wafers, where the trenches serve to define the positions and shapes of transferred NWs. Studies using semicircular trenches yield U-shaped NWs, with the x – y coordinates and radius of curvature defined ±20, ±40 and ±40 nm, respectively. Using standard photolithography, we implemented this methodology for wafer-scale deterministic assembly of U-shaped NWs with yields of ~90% for >430,000 sites. We applied this approach to assemble U-shaped NWs directional optical couplers that function as integrated nanoscale photonic circuit elements. Shape-controlled deterministic NW assembly enables new opportunities by combining strengths of top-down fabrication with diverse and tunable properties of one-dimensional building blocks in novel structural configurations at the wafer scale.

Our assembly method (Figure 4.1A and Appendix 18) involves two key steps. First, trenches with designed shapes are patterned in a surface layer on the target substrate. Second, the
NW growth substrate is translated with a fixed normal load and specific orientation with respect
to the trenches over the target substrate. During this latter “anchor-bend-align” process (Figure
4.1A) the trench structures serve to anchor and guide the bending of NWs during the shear
transfer process with overall alignment determined by translation.

**Figure 4.1** Shape-controlled NW assembly. (A) Schematics of deterministic assembly of U-
shaped NW arrays. The arrow shows the sliding direction of the NW growth substrate with
respect to the target substrate. (B) Photograph and optical images of wafer-scale
deterministically assembled U-shaped silicon NW arrays by trenches. NW diameter is 80 nm.
Figure 4.1, Continued: The arrow in (i) shows the sliding direction of the NW growth substrate with respect to the target substrate. Scale bars in (i)-(iii) are 10 mm, 200 µm and 50 µm, respectively. (C) Representative SEM image of U-shaped silicon NW array. Scale bar, 20 µm. (D) NW anchoring yield versus trench (i) width and (ii) depth. For (i), trench depth is fixed at 260 nm; for (ii), trench width is fixed at 3 µm. The blue vertical dashed line in (ii) corresponds to the 80 nm diameter NWs used in the measurements. Statistics are based on an area of 1.5×1.5 mm², 1,500 sites.

4.2 Results and Discussion

A prototypical example of our concept is shape-controlled deterministic assembly of U-shaped NWs as it captures all of the essential elements of the assembly process; that is, the U-shape structure requires assembly to define the radius of curvature, position and alignment. We first explored the capabilities of our approach in wafer scale deterministic assembly. First, photolithography was used to define >430,000 U-shaped trenches in 9 arrays on a 3 inch wafer, where the trench radius of curvature and depth were 1.5 µm and 260 nm, respectively (see Appendix 18). This patterned target substrate was mounted on a linear translation stage, coated with high viscosity mineral oil, and then the NW growth substrate (straight silicon NWs: lengths, 40–80 µm; mean diameter, 80 nm) was placed on the target substrate. After setting the pressure between the patterned target and NW growth substrates (~4.8 N cm⁻² in this experiment), the target substrate was translated in a direction perpendicular to the tangent of the U-shape (red arrow, Figure 4.1B) at a constant velocity.

Optical microscopy and scanning electron microscopy (SEM) images of the assembled NW arrays (Figure 4.1B,C) show several important features. First, U-shaped NWs are uniformly assembled on the patterned regions of the whole wafer with pitch of adjacent NWs of 15 µm and
row-to-row pitch of 100 µm. The overall assembly yield is ~90% (260 nm trench depth, statistics in an area of 1.5×1.5 mm², 1,500 sites). Specifically, ~60% of the trenches contain a single NW, ~20% two NWs, ~10% three NWs, and ~10% are vacant. Second, NWs are precisely anchored in the U-shaped trenches. The average offsets of x- and y- coordinates of NWs (U-shaped segments) are within ±20 and ±40 nm, respectively, from the trench edges, where the x-axis is the sliding direction. Third, NWs are precisely bent and aligned along the inner edge of the trenches. The average deviation of NW radius of curvature is within ±40 nm and the end segments of NWs are aligned within ±1°. Overall, these results demonstrate high-precision shape-controlled deterministic NW assembly on a wafer scale. In addition, it is important to note that the position and radius of curvature are fixed by the inner edge of the trenches, and thus it is not necessary to define nanometer width trenches to match the NW diameters in order to achieve precise assembly.

We assembled NWs in U-shaped trenches with varying width and depth to determine how these parameters affect assembly yield (Figure 4.1D). First, the yield increases with trench width, with a maximum of ~90% for widths ≥2 µm. Second, we observed that when trench depth is less than the NW diameter, the anchoring yield is close to zero, but that the yield increases to a maximum of ~90% for depths ≥ ~3 times the NW diameter. However, the highest yields with deeper trenches come at the cost of ca. 30% of the occupied sites containing 2 or 3 NWs (see above). To address this issue, which could affect applications of the assembly process, we examined the single/multiple NW yields at intermediate trench depths. For example, comparison of previous 260 nm and intermediate 130 nm trench depths shows that the single/multiple yield ratios increase from 2:1 to 6:1, respectively, although the total yield decreases only from 90 to 70%. These results indicate that mechanical ‘snagging’ rather than surface adhesion is
responsible for initial anchoring of NWs, and in the “anchor-bend-align” process, shear forces produced during the linear transfer (3,9,17) bend the NWs around the trench structural shape and align their arms to the transfer direction.

We conducted experiments and modeling to understand the mechanism and bending limits of shape-controlled assembly. SEM images of 80 nm diameter NWs assembled in trenches with radii of curvature from 1 to 3 μm (Figure 4.2A) show that the NW curvature matches that of the trenches with an average deviation ±40 nm; we address lower limits versus NW diameter below. We have investigated the effects of strain during assembly by using a focused ion beam (FIB) to cut one arm of suspended U-shaped NWs (Appendix 18). An in situ SEM video recorded during the cutting process (Supplementary Video 1 and Appendix 23), and transmission electron microscopy (TEM) images of suspended U-shaped NWs before and following FIB cutting (Figure 4.2B) reveal that NWs spring back to nearly straight configurations after the cutting process, thus indicating that bending is largely elastic for these conditions. High-resolution TEM images of suspended 80 nm diameter NWs with 3, 1.5, and 0.8 μm radii of curvature (Appendix 19) show that dislocation density in the curved portions of the NWs increases with reduced radius of curvature. This observation suggests that although strain in the NWs is largely elastic, inelastic deformation does occur in the NWs. These results are comparable to previous NW studies at high strain levels (24).
Figure 4.2 Characterization and mechanism of shape-controlled assembly. (A) Plot of the radius of NW curvature versus the trench radius of curvature. NW diameter is 80 nm. Insets: Representative SEM images of U-shaped silicon NWs assembled by U-shaped trenches with controlled radius, R, of curvature: (i) 1 µm; (ii) 2 µm; (iii) 3 µm. NW diameter is 80 nm. Scale bars, 2 µm. (B) Representative TEM images of U-shaped silicon NW (R = 1.5 µm) before (left) and after (right) cutting NW with an FIB. Scale bars, 1 µm. (C) Plot of full width at half
Figure 4.2, Continued: maximum (FWHM) of the first-order Raman scattering mode versus R of assembled U-shaped silicon NWs. Inset: Normalized Raman spectra acquired on silicon NWs: (i) straight/unbent NW; (ii-iv) U-shaped tip with R = 3.0, 1.5, and 0.8 μm, respectively; and (v) ~straight NW following FIB cutting on arm remote from bend (R = 1.5 μm prior to cutting). (D) Plot of silicon NW R versus contact pressure. Left inset: Model and force analysis of NW bending during assembly. Right inset: Plot of strain of silicon NWs versus contact pressure. NW diameters are 80 nm. (E) Plot of minimum R versus NW diameter under standard assembly conditions (pressure = 4.8 N cm$^{-2}$). Left inset: Plot of NW strain versus diameter. Right inset: Representative SEM image of U-shaped silicon NW assembled around a gold nanoparticle. NW diameter is ~10 nm. Scale bar, 200 nm.

We have further investigated the nature of the strained U-shaped NWs using Raman spectroscopy (Appendix 18). Representative spectra from 80 nm diameter individual straight, U-shaped with radii of curvature from 3 to 0.8 μm, and released straight NWs (inset, Figure 4.2C) reveal first-order scattering peaks centered at ~520 cm$^{-1}$ consistent with bulk Si. The full width at half maximum (FWHM) of this mode increases from 3.1 ± 0.2 cm$^{-1}$ (± 1 standard deviation (s.d.); N = 5; Figure 4.2C) in straight NWs to 7.0 ± 0.6, 10.9 ± 2.4, and 14.9 ± 3.1 cm$^{-1}$ as the U-shaped radius of curvature decreases to 3, 1.5, and 0.8 μm, respectively (N = 5; Figure 4.2C). Interestingly, following release by FIB-cutting, the FWHM returns to a value 3.3 ± 0.3 cm$^{-1}$ (N = 5) similar to unstrained NWs, and is thus consistent with SEM and TEM results described above. Previous studies (23) indicate that the increases in FWHM can be attributed to compressive (positive frequency shift) and tensile (negative shift) strains present in the U-shaped NWs.

We also studied the effect of contact pressure on NW curvature by transferring 80 nm diameter NWs into trenches with small ~200 nm radii of curvature. SEM images (Appendix 20) and analyses (Figure 4.2D; N = 10) for NWs assembled with contact pressures of 0.8, 4.8 and 7.2
N cm$^{-2}$ yield radii of $1500 \pm 85$, $800 \pm 100$ and $550 \pm 120$ nm and estimated strains (Figure 4.2D, inset) of 2.7, 5.0 and 7.3 %, respectively. Mechanical simulations (Appendix 20) show that for NWs fixed at one end, the radius of NW curvature decreases (strain increases) with increasing in-plane force ($F_{\text{load}}$), and are thus consistent with the proposal that increasing contact pressure during transfer yields increased shear force during the bending phase of assembly.

Last, we characterized the minimum radius of curvature as a function of NW diameter using a fixed contact pressure of 4.8 N cm$^{-2}$. A summary of results for assembly of U-shaped NWs with diameters of 10, 30 and 80 nm (Figure 4.2E, $N = 10$) yields minimum radii of curvature $100 \pm 50$, $400 \pm 80$ and $800 \pm 100$ nm and estimated strains of 5.0, 3.8 and 5.0 %, respectively. These results show that smaller diameter NWs achieve smaller radii of curvature for fixed contact pressure, and thus are consistent with anchor-bend-align assembly mechanism during linear translation of the growth/target substrates.

Shape-controlled NW assembly was used to assemble and characterize a directional nanophotonic light coupler (25) (Figure 4.3A) consisting of U-shaped and tangent straight NWs with a controlled gap. Schematically, when light is coupled into one end of the U-shaped (straight) NW, propagating light enters the coupling region and is directionally coupled into the tangent straight (U-shaped) NW. First, finite-difference time-domain (FDTD) simulations and measurements on a single U-shaped CdS NW waveguide component with radius of curvature 2 µm and 150 nm diameter (Appendix 21) show that NWs of this diameter support a fundamental waveguide mode at the CdS emission wavelength (~515 nm), and that this mode propagates from one straight arm, through the U-shaped section to the end of the other arm. Second, FDTD simulations of a U-shaped/tangent-straight directional coupler with a 70 nm gap (Figure 4.3B)
confirm efficient light coupling can be achieved with direct transmission and crossover coupling efficiencies of ca. 57 and 41%, respectively, and an estimated loss <3%.

**Figure 4.3.** NW directional photonic coupler. (A,B) Schematics (A) and calculated electric field intensity distributions (B) of a coupled waveguide system consisting of the U-shaped and straight CdS NWs with two different excitation schemes and light coupling mechanisms. Locations of excitation are at one end of the U-shaped (i) or the straight (ii) NWs. NW diameters, radii of curvature, and gap size were 150 nm, 4 μm, and 70 nm, respectively. Scale bars in (B), 4 μm. (C) Photoluminescence images of waveguiding and directional light coupling between U-shaped and straight CdS NWs. The red and yellow arrows indicate the locations at which the NW was optically pumped and the waveguided light was scattered, respectively. Excitation locations were
Figure 4.3, Continued: at one end of the U-shaped (i) or the straight (ii) NWs, respectively. Scale bars, 10 µm.

Significantly, optical studies of an assembled U-shaped/tangent-straight CdS NW structure with a 70 nm gap (Figure 4.3C) show that light emitted from the ends of the U-shaped and straight NWs in the two excitation geometries examined in FDTD simulations reveals consistent directional crossover coupling; that is, U-shaped to straight and straight to U-shaped. Quantitative analyses of the emission intensities at the two indicated NW ends yielded direct-to-crossover coupling ratios of ~2.7 (~2.0) for the two excitation geometries that differ somewhat from simulation (1.4). We attribute these differences to non-ideal shape and end facet configuration of the two assembled NWs, and believe that optimization of CdS NW synthesis and assembly will reduce such deviations in the future. Notably, using more uniform silicon NWs we have confirmed that the two-step process can be used to assemble U-shaped/tangent-straight structures with controlled gap sizes (e.g., 70 and 140 nm, Appendix 21), where FDTD simulations (Appendix 22) show that the directional coupling efficiency can be readily controlled by the gap distance in this regime. Hence, these results indicate that shape-controlled assembly represents a promising method for exploring photonic circuit fabrication in the future.

4.3 Conclusions

In summary, we have demonstrated a new concept of wafer-scale, high-precision shape controlled deterministic assembly of NWs. The positions and shapes of NWs can be simultaneously controlled during NW assembly. Taking advantage of this shape-controlled NW assembly technique, we developed high-density U-shaped NW arrays and assembled directional NW optical couplers. Compared to previous NW and carbon nanotube assembly techniques (1-
that have focused on straight one-dimensional structures, our shape-controlled assembly methodology opens up distinct research opportunities based on integrated nanodevices built from shape-controlled NWs with unique functions and properties. Examples of particular promising applications for further development include U-shaped NW bioprobe arrays for recording electrical and/or chemical signals from cells and tissues (26,27), and new functional integrated nanodevices based on NW strain-engineering (28,29).

4.4 References

Chapter 5: Deterministic assembly of strained germanium nanowires yields enhanced and tunable near infrared emission

There is substantial interest in strained germanium (Ge) as a silicon-compatible near infrared (NIR) photonic material, since it is predicted that tensile strain can yield a direct band gap in Ge. However, bulk Ge is incapable of sustaining sufficient strain without the development of defects and/or fracture, which degrade optical performance. Ge nanostructures offer a solution to this problem, since their high surface to volume and aspect ratios enable them to sustain strains significantly greater than those achievable in bulk without fracture. Here, we show that NIR emission from Ge nanowires (NWs) deterministically strained to as much as 3.1% is significantly enhanced and red shifted compared to unstrained Ge NWs. We apply our recently reported “anchor-bend-align” assembly technique to pattern U-shaped Ge NWs with controlled radii of curvature and thus strains. Raman spectroscopy studies and geometric analysis suggest that assembly of NWs into U-shapes imparts compressive and tensile strain on the inner and outer edges, respectively, of the curved NWs. NIR photoluminescence (PL) imaging of single strained Ge NWs with diameters of 100 and 30 nm reveals strong light emission localized to the strained portions of the NWs which is enhanced by factors greater than 25 compared to unstrained segments of the NWs. Finally, PL spectroscopy shows that the NIR emission from single Ge NWs can be monotonically tuned from ~1550 to 1900 nm by deterministically adjusting the radius of curvature and/or the diameter of the NWs. Enhanced and deterministically tunable red shifted NIR emission from low-footprint strained Ge structures suggests promising application of curved Ge NWs in silicon-compatible optical communications and photonics.
5.1 Introduction

Photonic elements integrated with microelectronics present advantages such as more rapid data transmission speeds, increased density of computing elements and interconnects, and decreased power consumption over traditional metallic interconnects (1). Currently, there is substantial interest in Ge as a photonic material since it is compatible with complementary metal oxide semiconductor processing techniques (2,3). Ge has been applied for NIR and mid-IR photodetectors, waveguides, window materials, and electro-optical modulators (2-4). However, Ge has an indirect band gap, rendering it an inefficient light emitter.

The electronic band structure – and thus optical properties – of Ge can be modified via the application of strain. In unstrained Ge, the valence band maximum at the Γ point and the conduction band (CB) global minimum at the L point yield an indirect band gap of 0.66 eV (1879 nm). A local minimum in the CB at the Γ point, offset ~136 meV higher than the L point CB minimum, yields a direct gap at 0.8 eV (1550 nm). This overall indirect band structure renders Ge an inefficient light emitter because of preferential carrier occupation of the CB minimum at the L point. However, it is predicted that sufficient tensile strain – from ~2-5% depending on the crystal direction(s) in which strain is applied (5-8) – can yield a direct band gap in Ge by lowering the energy of the CB minimum at the Γ point relative to the CB minimum at the L point. Such an effect expands the spectral energy range over which Ge is sensitive to incident photons and enhances the rate of radiative recombination at the Γ gap relative to other carrier relaxation pathways to enable efficient light emission.

Bulk Ge is incapable of sustaining sufficient strain without the development of defects and/or fracture, which degrade optical performance (2,3,9). Ge nanostructures are a promising material platforms in which to strain Ge, since their high surface to volume and aspect ratios
enable them to sustain strains significantly greater than those achievable in bulk without fracture (9). A variety of methods for applying strain to Ge nano- and micro-structures have been demonstrated to alter the optical properties of Ge, including growth of Ge thin film waveguides on lattice-mismatched substrates (10-12), bending Ge nanomembranes released from Ge-on-insulator (GOI) wafers (13), and fabrication of narrow GOI (or Ge-Sn alloy) nano- (14) and micro-bridges (15-18).

NWs can also sustain significant strains. For instance, Ge NWs with diameters of 100 and 30 nm were shown to sustain strains up to ~4 and 15%, respectively, before fracture (19). Additional studies of CdS (20,21) GaAs (22,23), ZnO (24-26), and Si (27) NWs have demonstrated that curvature-induced strain can tune the optical properties of these NWs. Furthermore, photodetectors fabricated from single Ge NWs under tensile strain were shown to be more responsive than unstrained NWs to photons with wavelengths longer than 1550 nm, consistent with a reduction in the direct band gap energy of the NW (28,29). However, to our knowledge, light emission from single, strained Ge NWs has not been characterized despite its technological significance. Here, we present the first systematic characterization of the optical emission properties of single, deterministically strained Ge NWs.

5.2 Results and Discussion

Our approach to characterizing the strain-dependent optical properties of Ge NWs consists of three steps which are detailed in Chapter 4. In summary, first, Ge NWs of a given diameter, D, were synthesized by gold (Au) nanoparticle catalyzed growth (Appendix 24) (30). Second, an Au receiving substrate was patterned with 250 nm deep U-shaped trenches (Appendix 24). Finally, Ge NWs were assembled into U-shapes using our recently reported “anchor-bend-align” transfer printing assembly technique (31) (Figure 5.1A), in which NWs
were shear transferred from a growth substrate to the patterned receiving substrate (Appendix 24). The dimensions of the U-shaped trenches, including the radius of curvature, $\rho$, were defined by photolithography (Figure 5.1A, right). We note that integrating bottom-up NW synthesis with top-down lithography enables tuning of D and $\rho$, respectively.
Figure 5.1 U-shaped Ge NW assembly. (A) Schematic depicting U-shaped NW assembly. Left, NWs are transferred from the growth substrate onto a receiving substrate patterned with U-shaped trenches in Au by translating the growth substrate relative to the receiving substrate in the direction depicted by the red arrow. Right, top-down view depicting D and ρ of the assembled U-shaped NWs. (B) Tilted SEM image of an Au U-trench with ρ = 4.4 µm prior to NW assembly.
Figure 5.1, Continued: Scale bar, 2 μm. (C) Left, tilted SEM image showing a Ge NW (false colored blue) with D = 100 nm following assembly in an Au U-trench with ρ = 4.4 μm. Scale bar, 2 μm. Right, high magnification SEM image of the area indicated by the red box. Scale bar, 1 μm. (D) Bright-field optical microscope images of Ge NWs with D = 100 nm assembled in Au U-trenches with ρ = 4.4, 3.3, 2.7, 2.1, and 1.6 μm. Scale bar, 10 μm.

Scanning electron microscope (SEM) images before (Figure 5.1B) and following (Figure 5.1C) assembly of Ge NWs with D = 100 nm reveal a NW adjacent to the walls of a U-shaped trench with ρ = 4.4 μm. Since previous studies have indicated that strain in NWs increases with decreasing ρ (20,24,25,27), trenches with additional ρ were fabricated and NW assembly was performed in the same manner. Bright-field optical microscope images (Figure 5.1D) reveal that NWs with D = 100 nm were successfully assembled into U shapes with ρ = 4.4, 3.3, 2.7, 2.1, and 1.6 μm. Together, these observations demonstrate that the ρ of Ge NWs can be systematically controlled by assembling NWs into lithographically defined U-shaped trenches.

To analyze light emission from these single curved Ge NWs, we performed wide-field and micro-PL (μ-PL) imaging and spectroscopy using a custom-built, far-field epifluorescence microscope equipped with a 2-dimensional InGaAs charge-coupled device (CCD) with upper efficiency cutoff at 1700 nm and a 1-dimensional InGaAs spectrometer with upper efficiency cutoff at 2100 nm (Appendices 24 and 25). A wide-field PL image (representing wavelengths 1100-1700 nm) of a Ge NW with D = 100 nm assembled in a gold U-trench with ρ ~2.7 μm is shown in Figure 5.2A. The image reveals bright PL emission at the curved portion of the NW which is significantly more intense compared to PL emission from the straight sections of the NW. μ-PL spectra from straight and curved sections of the NW are plotted in Figure 5.2B and display two key features. First, emission from the straight segment is centered at ~1510 nm.
Comparison of this PL spectrum to previous studies suggests that this emission can be attributed to radiative recombination at the direct gap of Ge at ca. room temperature (32,33). Second, in contrast, the PL spectrum from the curved segment shows a peak centered at ~1800 nm. This emission from the curved portion is a factor of ~12 more intense than the emission from the straight portion of the NW at 1800 nm. We note that the same laser excitation power was used to excite both the curved and straight segments of the NW, suggesting that the red shift and PL enhancement do not result from laser-induced NW heating (33).
Figure 5.2 PL imaging and spectroscopy of Ge NWs with D = 100 nm. (A) Wide-field PL image of a NW assembled in an Au U-trench with $\rho = 2.7$ $\mu$m. Scale bar, 5 $\mu$m. Exposure time: 300 ms. (B) $\mu$-PL spectra from a straight (point 1; black squares) and curved (point 2; red circles) portion of the NW shown in (A). Exposure time: 300 ms. Each point represents the average of 5
**Figure 5.2, Continued:** exposures for a given wavelength. (C) PL peak wavelengths from NWs as a function of ρ. N = 25 NWs for the straight point and 5 NWs for the curved NW points; error bars denote ±1 standard deviation. The green triangle denotes the most red shifted emission observed from a single NW.

To characterize the influence of the curvature of the NWs on their PL, we assembled undoped, intrinsic Ge NWs with D = 100 nm in U-trenches with different ρ (Figure 5.2C). Emission from the straight sections of the assembled NWs is centered at ~1503 ± 75 nm (N = 25 straight NWs; ± 1 standard deviation (s.d.); labeled ‘straight’ in Figure 5.2C), in agreement with the above observation from a single NW. Average center emission wavelengths (energies) for the curved sections assembled with ρ = 4.4, 3.3, 2.7, 2.1, and 1.6 μm were 1615 ± 61 (0.77), 1681 ± 26 (0.74), 1773 ± 104 (0.70), 1726 ± 93 (0.72), and 1710 ± 80 (0.73) nm (eV), respectively (± 1 s.d.; N = 5 curved NWs for all measurements). For all 25 of the curved NWs which contributed to the averages in Figure 5.2C, we observe stronger emission from the curved portions than from the straight sections. Interestingly, we observe a similar trend in PL red shift vs. ρ for n-type phosphorous-doped Ge NWs (Appendix 26). Additionally, we note that the most red shifted emission that we observed for a single NW is centered at ~1892 nm (0.65 eV) for ρ = 2.1 μm, as denoted by the green triangle in Figure 5.2C. The emission at the curved portion of this NW is ~28 times more intense than emission at 1892 nm from the straight portions of the same NW. These PL results show that for Ge NWs with D = 100 nm, (i) PL emission centers from the straight segments of the NWs do not depend on ρ; (ii) NIR PL is enhanced by factors exceeding 25 at the curved portions of the NWs compared to the straight NWs and (iii) decreasing ρ yields emission which is monotonically red shifted up to ~1900 nm (~150 meV) until ρ < ~2.1 μm.
Therefore, we propose that the curvature induced during U-shaped assembly yields elastic strain in the NWs, which accounts for the systematically red shifted emission with decreasing $\rho$.

To better quantify strain in the U-shaped Ge NWs, we characterized the U-shaped Ge NWs with $D = 100$ nm with micro-Raman spectroscopy (Appendix 24). Representative spectra from straight (i) and curved (ii-iv) portions of single NWs with $\rho = 4.4, 3.3, 2.7, 2.1, \text{ and } 1.6 \, \mu m$ are plotted in Figure 5.3A. For all $\rho$, we observe Raman scattering peaks centered at $\approx 300 \, \text{cm}^{-1}$, which matches the peak center for Raman scattering from bulk, unstrained Ge (34). The full-width half maximum (FWHM) for the Raman scattering peak from straight NWs is $3.17 \pm 0.37 \, \text{cm}^{-1}$ ($\pm 1$ s.d.; $N = 5$ straight NWs). In contrast, Raman scattering spectra reveal systematic increases in peak FWHM for decreasing $\rho$ (Figure 5.3B): $4.04 \pm 1.19, 4.54 \pm 0.50, 5.08 \pm 1.31, 5.22 \pm 0.98, 5.84 \pm 0.81 \, \text{cm}^{-1}$ ($\pm 1$ s.d.; $N = 5$ curved NWs for all measurements) for $\rho = 4.4, 3.3, 2.7, 2.1, \text{ and } 1.6 \, \mu m$, respectively.
Figure 5.3 Raman spectroscopy of Ge NWs with D = 100 nm. (A) Representative Raman spectra from (i) straight Ge NWs and the (ii-vi) curved portions of NWs assembled with \( \rho = (ii) \).
Figure 5.3, Continued: 4.4, (iii) 3.3, (iv) 2.7, (v) 2.1, and (vi) 1.6 μm. (B) Raman scattering peak FWHM as a function of ρ. N = 5 NWs for all data points; error bars denote ±1 standard deviation.

To rationalize our experimental Raman observations, we consider previous studies of curved NWs, which indicate that the inner radius of a curved NW undergoes compressive strain whereas the outer radius undergoes tensile strain (20,24,25,27). Since the laser spot used for Raman spectroscopy (D ~ 1 μm) is larger than the NWs (D = 100 nm), Raman spectroscopy samples both inner and outer regions of the curved NWs. Compression (tension) yields a blue (red) shift in the frequency of Raman scattering (35). Therefore, the broadened Raman scattering peaks suggest both compressive and tensile strained regions in the curved NWs (36). Moreover, increasing FWHM of the Raman peak with decreasing ρ (Figure 5.3B) suggests that NWs assembled with smaller ρ sustain increasing levels of compressive (tensile) strain at their inner (outer) edges.

Next, we consider the effect of compressive (tensile) strain at the inner (outer) edges of curved NWs on their band structure and PL properties. Qualitatively, in a semiconductor, compressive (tensile) strain widens (narrows) the band gap; this principle suggests a wide-to-narrow energy gradient from inner to outer radius (Appendix 27) (37). After carriers are excited within the NW, they relax to the outer (narrow band gap) edge of the NW and recombine, yielding PL emission (20,24,25). This is feasible in Ge NWs since carrier diffusion lengths have been shown to be at least an order of magnitude larger than Ge NWs’ diameter (38,39). Therefore, the energy of photons emitted via band-edge recombination PL in curved NWs is dependent on the tensile strain at the outer edge of the NWs.
This tensile strain at the outer edge of a curved NW in which $\rho$ is significantly larger than $D$ can be approximated (Appendix 24) as

$$\varepsilon_{\text{tensile}} = \frac{D}{2\rho}$$

(1)

Therefore, by equation (1), Ge NWs with $D = 100$ nm assembled with 4.4, 3.3, 2.7, 2.1, and 1.6 $\mu$m sustain $\varepsilon_{\text{tensile}} = \sim 1.1$, 1.5, 1.9, 2.4, and 3.1% tensile strain at their outer diameter. With increasing tensile strain due to decreasing $\rho$ up to $\varepsilon_{\text{tensile}} < \sim 2.4\%$, we observe a monotonic red shift of the average emission center from $\sim 1500$ (0.82) to 1775 nm (0.70 eV) (or, in the case of single NWs, up to $\sim 1900$ nm). These PL and Raman studies suggest that by tuning $\rho$ for 100 nm Ge NWs, we can tune the strain in the NWs, enabling deterministic adjustment of the NIR emission center over $\sim 150$ meV. Furthermore, these results are consistent with (i) a relative lowering of the CB minimum at the $\Gamma$ point compared to the minimum at the L point in strained Ge as well as (ii) excited carriers relaxing to and radiatively recombining at the most highly strained outer edges of the NWs. Interestingly, at $\varepsilon_{\text{tensile}} > \sim 2\%$, the average emission center blue shifts, although this blue shift is not statistically significant within one s.d. Thus, we hypothesize that for NWs with $D = 100$ nm, around $\varepsilon_{\text{tensile}} > \sim 2.4\%$, the defect density increases due to the strain (31,40). Since defects act as recombination centers in Ge (2,9) we propose that these strain-induced defects prevent excited carriers from relaxing to the outer edge of the NWs, thereby reducing the rate of radiative recombination at the highly strained outer edge of the NW relative to recombination at other (less-strained) sites.

To test the above analysis, we characterized the curvature-dependent NIR PL properties of Ge NWs with smaller Ds, since assembly of NWs with $D < 100$ nm but the same $\rho$ should yield a lower strain according to equation (1), and thus a different PL emission peak center. To
this end, Ge NWs with \( D = 30 \) nm were assembled in Au U-trenches in a manner similar to what was described above. A PL image (representing emitted photons with wavelengths 1100-1700 nm) of a Ge NW assembled with \( \rho = 0.85 \ \mu m \) (\( \varepsilon_{tensile} \approx 1.8\% \), by equation (1)) (Figure 5.4A) reveals localized, intense emission at the curved portion of the NW. PL spectra from the straight and curved segments are centered at 1565 and 1738 nm, respectively (Figure 5.4B). The emission at the curved region is enhanced relative to that from the brightest portion of the straight NW section by a factor of ~8. Finally, we characterized the influence of curvature (and thus strain) on the 30 nm diameter NWs (Figure 5.4C) assembled in trenches with other \( \rho \). For \( \rho \) (\( \varepsilon_{tensile} \)) = 4.4 (0.3), 3.3 (0.5), 2.7 (0.6), 2.1 (0.7), 1.6 (0.9), 1.1 (1.4) \( \mu m \) (%), PL emission centers from the curved portions of the NWs are located at 1550 (0.80), 1592 (0.78), 1601 (0.77), 1640 (0.76), 1663 (0.75), and 1706 (0.73) nm (eV), respectively. Indeed, these PL spectroscopy results from Ge NWs with \( D = 30 \) nm reveal a monotonic red shift of emission center from 0.80 to 0.71 eV with increasing \( \varepsilon_{tensile} \). Based on PL results from NWs with both \( D = 30 \) and 100 nm (Appendix 28), we observe that the PL emission center as a function of \( \varepsilon_{tensile} \) by equation (1) – rather than as a function of trench geometry (e.g. \( \rho \) and trench width) – is nearly identical; or conversely, that the emission center is different for identical trench geometries for NWs with different Ds and thus strains. Substrate-based (e.g. plasmonic) influences on the PL red shift would depend strongly on geometrical factors such as \( \rho \) and the width of the Au U-trench (41). Therefore, this observation helps to rule out significant influence from the substrate on the PL emission center and further strongly suggests that curvature-induced strain in the NWs accounts for the observed red shift and enhancement of NIR PL emission.
Figure 5.4 PL imaging and spectroscopy of Ge NWs with D = 30 nm. (A) Wide-field PL image of a NW assembled in an Au U-trench with $\rho = 0.85 \mu$m. Scale bar, 10 $\mu$m. Exposure time: 300 ms. (B) $\mu$-PL spectra from the straight arm (point 1; black squares) and the curved portion of the NW (point 2; red circles) shown in (A). Exposure time: 300 ms. Each point represents the...
Finally, we compare our PL results to those reported previously. A best linear fit (Appendix 28) for average emission center energy, $E$, vs. $\varepsilon_{\text{tensile}}$ indicates that $E = -0.062\varepsilon + 0.82$ eV ($R^2 = 0.93$). We note that this rate of $\sim 60$ meV per % strain red shift of PL emission from the $\Gamma$ gap is quite similar to those reported previously of $\sim 40$-80 meV per % strain red shift in emission (14,17) or absorption edge (28,29) for strained Ge nanostructures in other geometries. Moreover, transmission electron microscopy (TEM) and selected area electron diffraction analysis (Appendix 29) indicates that the growth direction of the Ge NWs is $<110>$. The $<110>$ crystal growth direction matches that previously reported for Ge NWs grown with similar synthesis conditions (30). Band structure calculations for Ge strained uniaxially in the $<110>$ direction predict $\sim 60$ meV per % strain narrowing of the direct gap (7), similar to our observations. Together, these considerations further strengthen the conclusion that strain in the U-shaped NWs accounts for the NIR PL emission enhancement and systematic red shift.

5.3 Conclusions

In summary, we applied a shear transfer based deterministic assembly technique to pattern U-shaped Ge NWs with controlled $\rho$. PL characterization of single U-shaped Ge NWs with $D = 100$ and 30 nm revealed localized light emission at the curved sections enhanced by factors greater than 25 compared to the straight segments of the same NWs. Moreover, $\mu$-PL spectroscopy showed that tuning $\rho$ monotonically red shifts the NIR emission from the U-shaped sections of the NWs up to $\sim 1900$ nm (150 meV). Raman spectroscopy and a geometric analysis indicated that assembly of NWs into U-shapes imparted compressive and tensile strain on the
inner and outer radii of the curved NWs, respectively. Therefore, combining bottom-up synthesis and top-down photolithography to adjust $D$ and $\rho$, respectively, enables predetermined tuning of strain up to ~3.1% and, correspondingly, the optical properties of the Ge NWs. Enhanced and deterministically red shifted NIR emission from low-footprint strained Ge structures suggests promising application of curved Ge NWs in silicon-compatible optical communications and photonics.

5.4 References

31. Chapter 4.


Appendix 1

Experimental for Chapter 2

Nanowire Synthesis

Faceted Si nanowires (NWs) with diameters from 200 to 400 nm were grown according to a previously described procedure by depositing different thickness Si shells on ca. 100 nm diameter Si NW cores at 775-860 °C (1). The growth substrate with the faceted Si NWs was dipped in buffered hydrofluoric acid (BHF; 5173-03; J.T. Baker) for 20 s to remove surface oxide, rinsed for 5 s in deionized water, and then submerged in liquid nitrogen to freeze remaining water on the NW/substrate chip; this process prevents collapse of the low-density NWs via capillary forces during liquid water evaporation (1). The frozen growth substrate was quickly transferred to the second zone of a 3-zone furnace and the furnace was evacuated to a base pressure of 50 mTorr, as previously described (2). Once at base pressure, the furnace was purged three times each with Ar (semiconductor grade; Matheson Tri-Gas; 99.999%) and H₂ (ultrahigh purity; Airgas; 99.999%) and the pressure was set at ~2.8 Torr with a flow rate of 20 sccm H₂. The 3-zone furnace is equipped with a quartz boat with adjustable position using a quartz transfer rod. Prior to the above evacuation and purge, the quartz transfer boat was loaded with either CdS powder (-325 mesh; Alfa Aesar; 99.999%) or milled InP powder (Alfa Aesar; 99.9999%). Once the temperature of zone 1 stabilized at 670-710°C, the quartz rod was used to position the precursor in the center of zone 1. CdS or InP shells were grown on the Si NWs in zone 2 at 450-550°C for 5-40 minutes.

Electron Microscopy Characterization
NWs were imaged directly on the growth substrate using a Zeiss Ultra Plus field emission scanning electron microscope (SEM). For plan-view transmission electron microscope (TEM) or scanning TEM (STEM) imaging, NWs were mechanically transferred from the growth substrate to amorphous-carbon coated copper TEM grids (Ted Pella). Cross-sections were prepared by deposition of a protective carbon layer and subsequent lift-out using a Zeiss NVision 40 dual-beam SEM/focused ion beam (FIB) equipped with an Omniprobe micromanipulator. Both the plan-view and cross section NW samples were characterized using an aberration-corrected Zeiss Libra MC TEM operating at 200 keV. STEM-based energy dispersive x-ray spectroscopy (EDS) elemental mapping characterization was completed using an aberration-corrected Hitachi HD-2700 STEM operating at 200 keV.

**Optical Characterization**

Photoluminescence images were recorded at room temperature using a scanning confocal microscope (FluoView FV1000; Olympus America Inc.) with 473 nm excitation and a 490-540 nm band pass filter to pass photoluminescence and block excitation laser light. Optical spectroscopy at room temperature utilized a home-built epifluorescence microscope (3). A continuous-wave 405 nm diode laser (LaserGlow Technologies) was collimated and focused to a ~1 µm diameter spot with incident power ~900 µW using a 40x objective lens (NA = 0.75; Olympus America Inc.). The laser and luminescence were passed through a 405 nm dichroic and subsequently through two 450 nm long pass filters to remove excitation light and finally to a 150 mm spectrometer (SP150; Princeton Instruments; 300 lines mm\(^{-1}\) grating) equipped with a CCD detector (NTE 2; Roper Scientific).
Appendix 1 References


Appendix 2

Figure A2.1 Yield of facet-selective Si/CdS heterostructure NWs. Top, SEM image of a region of a typical growth substrate in which CdS was grown facet-selectively on every NW in the field of view. Scale bar, 20 µm. Bottom, four high resolution SEM images of facet-selective Si/CdS heterostructure NWs as denoted in the wide-view image above by I, II, III, and IV. Scale bars, 1
Figure A2.1, Continued: µm. Facet-selective CdS growth occurs on >95% of faceted Si NWs on the downstream end of the growth substrate.
Appendix 3

Figure A3.1 Additional characterization of the Si-CdS heterostructure NWs. (A) Schematic depicting the locations from which the cross-sectional TEM images in (B) and (C) were recorded. (B) Fourier-filtered TEM image of the region of the Si-CdS \{111\} interface shown in Figure 3B derived from the CdS<0110> reflection. Scale bar, 5 nm. The image reveals misfit dislocations (red arrows) ~4 nm from the Si-CdS interface (dashed red line). (C) Cross-sectional TEM image of the CdS grown on the \{111\} facet of a Si NW ~100 nm from the Si-CdS \{111\} interface. Scale bar, 5 nm. The TEM image reveals that the CdS in this region is practically free
Figure A3.1, Continued: of defects, suggesting that despite the initial formation of misfit dislocations near the interface, the majority of the CdS has high crystalline quality.
Appendix 4

Figure A4.1 CdS growth on faceted Si NWs without removing the Si native oxide prior to growth. SEM images of (A) upstream and (B) downstream Si/CdS heterostructure NWs grown without a BHF etch prior to CdS deposition. Upstream, the CdS deposits conformally on the NWs but lacks the well-developed surface facet seen in the NWs grown with BHF etch prior to CdS deposition as in Figure 3; downstream, no continuous CdS shells deposit on the Si NWs, in contrast to those shown in Figure 1. Scale bars, 1 µm.
Appendix 5

Experimental for Chapter 3

Periodic Shell Nanowire (NW) Synthesis

Si periodic shell NW growth: Au nanoparticle catalysts (20, 30, 50, 80, and 100 nm; Ted Pella) were diluted 1 to 100 by volume in water and subsequently dispersed on an oxidized Si growth chip (p-type Si, 0.005 Ω cm, 600 nm oxide; Nova Electronic Materials) functionalized with 0.1% w/v poly-L-lysine (150,000 – 300,000 g/mol; Sigma Aldrich) in water. After rinsing in deionized water and drying with nitrogen, the substrates were placed into a home-built chemical vapor deposition reactor and the system was evacuated to a base pressure of ~5 mTorr. Si core NWs were grown via the Au nanoparticle catalyzed growth mechanism (1) for ~10-60 minutes at 465°C and a total pressure of 40 Torr with 1 standard cubic centimeter per second (sccm) silane (SiH₄; 100%; Voltaix) and 60 sccm hydrogen (H₂; 99.999%; Matheson) flow rates. Following core growth, the furnace temperature was ramped to 700-850°C for shell growth. At this temperature, shells were grown for 1-60 minutes at ~0.3 Torr with gas flow rates of 0.15-10 sccm SiH₄ and 0-200 sccm H₂. For some syntheses, phosphine (PH₃, 1000 p.p.m. in H₂; Voltaix) was introduced to the reactor during shell growth at 0.5-20 sccm flow rates. Ge periodic shell NW growth: Germanium core NWs were typically synthesized from 50 nm Au nanoparticle catalysts at a total pressure of 300 Torr with 200 sccm H₂ and 20 sccm germane (GeH₄; 10% in H₂; Voltaix) flow rates. Ge cores were nucleated for 5 minutes at 330°C and grown for another 50 minutes at 270°C. For heterostructure growth, Si cores were grown in the same way as described for Si shells on Si cores. Ge periodic shells were grown on the Si cores by increasing
the temperature to 450 – 600°C and decreasing the pressure to ~0.3 Torr with GeH₄ flow rates of 1-40 sccm.

**NW Characterization**

End-on view scanning electron microscopy (SEM, Zeiss Ultra Plus field emission SEM) images of periodic shell NWs were recorded directly from the as-synthesized growth wafers. For plan-view SEM images and NW pitch measurements, NWs were transferred to Si₃N₄-coated Si wafers (200 nm Si₃N₄, 100 nm SiO₂ on p-type Si, 0.005 Ω cm; Nova Electronic Materials). Transmission electron microscopy (TEM) and diffraction samples were prepared by shear transfer methodology (2) on amorphous carbon-coated copper TEM grids. The samples were imaged directly in JEOL 2100 or JEOL 2010F field emission high resolution TEMs operating at 200 keV. High-angle annular dark-field scanning TEM (HAADF-STEM) imaging and analysis was performed on an aberration corrected Zeiss Libra 200 MC operating at 200 keV. Energy dispersive X-ray spectroscopy (EDS) maps were collected at 512 x 400 resolution using a 400 ms dwell time per pixel in commercial EDAX Genesis software. Optical dark field images of NWs on silicon nitride-coated substrates were recorded using an Olympus BX51 microscope.

**Relative stability of periodic shell NWs**

To obtain a qualitative understanding of the stability of different periodic shell structures, we have compared the surface areas of different 1D configurations. We assume that surface energies of NWs can be approximated by their surface areas (3,4). The periodic shell NWs were modeled as adjoining cylinders of lengths L_{inner} and L_{outer} and diameters D_{inner} and D_{outer}; one inner and one outer cylinder define a unit cell. We assume the additional volume is added, V_{added},
to the outer shell and that $D_{\text{inner}}$ is unchanged and corresponds to the original diameter of the NW core:

$$V_{\text{added}} = V_{\text{outer}} - V_{\text{core}} = \frac{\pi L_{\text{outer}}}{4} (D_{\text{outer}}^2 - D_{\text{core}}^2)$$

(1)

In Appendix 15, we consider the specific case in which $V_{\text{added}}$ is constant and pitch is fixed at 3 $\mu$m but modulation amplitude is not fixed. $V_{\text{added}}$ was obtained from dimensions of a typical periodic shell NW measured by SEM ($L_{\text{inner}} = 1,500$ nm, $L_{\text{outer}} = 1,500$ nm, $D_{\text{inner}} = 100$ nm, $D_{\text{outer}} = 300$ nm, and total length, $L_{\text{total}} = 30$ $\mu$m). If this $V_{\text{added}}$ were distributed uniformly along the NW axis, the NW would have a uniform diameter along its axis of

$$D_{\text{straight,equiv}} = \left( \frac{4(V_{\text{added}} + V_{\text{core}})}{\pi (L_{\text{inner}} + L_{\text{outer}})} \right)^{\frac{1}{2}}$$

(2)

For these dimensions, $D_{\text{straight,equiv}} = \sim 223.6$ nm. The surface area of the periodic shell to the surface area of the straight NW is $SA_{\text{Periodic}}/SA_{\text{straight,equiv}}$.

We determine the surface areas of NWs with different modulation amplitudes by varying $L_{\text{outer}}$ (and thus $L_{\text{inner}}$, since $L_{\text{outer}} + L_{\text{inner}} = \text{pitch} = 3,000$ nm) for $20$ nm $< L_{\text{outer}} < 3,000$ nm in increments of $20$ nm. Since $V_{\text{added}}$ is constant, $D_{\text{outer}}$ must also change with $L_{\text{outer}}$. For every $D_{\text{outer}}$, we calculate the surface area. Absolute surface area values can be compared for a given $D_{\text{outer}}$ or dimensionless comparisons can be made with ratios of periodic shell surface areas to straight NW surface areas for a given diameter modulation (where diameter modulation $= D_{\text{outer}}/D_{\text{inner}}$, and $D_{\text{inner}}$ is constant here at 100 nm). See Appendix 15 for additional calculations of surface area vs. diameter modulation with different values of $V_{\text{added}}$. 

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For consideration of surface area vs. pitch (Figure 3.2C), we expand the above calculation by considering pitches ranging from 500 nm to 15 μm in increments of 100 nm; for the general case with different pitches, there are \( n = \frac{L_{\text{total}}}{\text{pitch}} \) unit cells per NW and the volume is distributed evenly among the \( n \) outer shells. We perform the analysis for each pitch to produce surface areas as a function of diameter modulation and the minimum surface area for a given pitch is then plotted as a function of surface area vs. pitch. See Appendix 15 for additional calculations of surface area vs. pitch with different values of \( V_{\text{added}} \).

This simple geometric analysis is material-independent and dimensionless, and as expected, shows that periodic shell NWs can have reduced surface energies compared to uniform diameter NWs of equivalent volume.

We have also performed a similar analysis with the cross sectional morphologies and specific Si surface facets experimentally observed in periodic shell growth (Appendix 15). We use the same \( V_{\text{added}}, L_{\text{inner}}, L_{\text{outer}}, \) and pitch that we applied to the above cylindrical cross-section calculations. Then, we compute the surface energy for the periodic shell NWs with experimentally observed cross sections (Appendix 16) with a variety of diameter modulations and cross sectional aspect ratios and compare it to the surface energy of a uniform-diameter NW of equivalent volume and cross sectional aspect ratio. Surface energy (SE) is defined as \( \text{SE} = \sum A_i \gamma_i \), where \( A_i \) is the area of surface \( i \) and \( \gamma_i \) is its surface energy density. We use surface energy densities of 88.6 and 94.8 meV/Å² for the Si{111} and {113} surfaces, respectively (5). The angles between facets were defined by the crystallographic properties of Si and closely match the angles between facets observed in end-on SEM images of faceted periodic shell NWs (i.e. 60.5° and 119.5° between adjacent {113}/{113} and {111}/{113} facets, respectively). For the transitional facets (the crystal faces between the inner and outer shells), we assume the
average surface energy of the \{111\} and \{113\} surfaces. Importantly, we find that the periodic shell NWs with experimentally-observed cross sections have reduced surface energies compared to uniform diameter NWs of equivalent volume and cross sectional aspect ratio. These results are similar to our calculations of relative stabilities (periodic shell vs. uniform) based on surface area analysis.

**Estimation of diffusion lengths**

For conditions similar to our experiments (i.e., SiH\textsubscript{4} partial pressures from ca. 1 to 40 mTorr, and temperature ranges from 735 to 855°C), Lim et al. estimate diffusion lengths of 70 nm, 140 nm, and 200 nm at 550, 600, and 650°C at SiH\textsubscript{4} partial pressures of 0.6 mTorr on the Si(100) surface (6). Given (1) that diffusion lengths increase exponentially with temperature (this holds true for temperatures < 900°C; for temperatures of 900-1000°C, diffusion lengths begin to decrease due to Si adatom desorption rates becoming appreciable), and (2) that diffusion lengths on Si (111) (i.e. our major surfaces) are approximately an order of magnitude higher compared to those on Si (100) (7), we estimate a lower limit for diffusion lengths of >200 nm to 2000 nm for shell deposition at the lower regime of temperatures used in our studies. Indeed, we begin to observe periodic shells with average pitch of 1.2 µm (Appendix 13) at 735°C and a SiH\textsubscript{4} partial pressure of 14 mTorr on 100 nm cores.

For higher temperatures and lower pressures, we can expect an increase in diffusion lengths until desorption becomes appreciable at temperatures >900°C. We are unable to perform periodic shell growth experiments at temperatures greater than 900°C as the underlying NW cores transform into isolated particles very quickly due to the Plateau-Rayleigh instability, as shown in Figure 3.1B. Although estimates for surface diffusion lengths of Si cannot be found for
CVD deposition with SiH$_4$ at temperatures approaching 900°C, we estimate an upper limit of diffusion lengths using values reported from studies on annealed (i.e. no growth) Si(111) and Si(100) surfaces. At 900°C, Si diffusion lengths have been estimated up to 10s of microns (8,9). This serves as an upper limit for our diffusion lengths at 855°C; that is, the diffusion length will be reduced for our growths due to incoming flux of SiH$_4$ molecules as well as lower temperatures.

In summary, we estimate diffusion lengths in the periodic shell growth regime to be > 200 nm at our lowest temperature of 735°C and 10s of microns at the highest temperature of 855°C used in our growth. This range encompasses the observed pitch range from our experiments (i.e. 500 nm to 10 µm).

Given that (1) our conservative lower limit of diffusion lengths suggests that diffusion lengths are on the order of our observed pitches, (2) that these diffusion lengths scale with temperature and pressure similarly to how periodic shell pitch scales with temperature and pressure, and (3) that it is known from literature that diffusion lengths are important factors for determining morphology at our CVD conditions using SiH$_4$ (3,6), it is reasonable to conclude that surface diffusion lengths contribute significantly to formation of periodic shells.

**Finite-Difference Time-Domain (FDTD) calculations**

Analyses were performed using incident plane waves with the transverse-electric (TE) polarization state normal to a single NW(substrate). In the calculations, the NW and substrate parameters are consistent with experimental values (e.g. substrates are 200 nm thick Si$_3$N$_4$/100 nm thick SiO$_2$). The absorption cross section of a NW was calculated using periodic and perfectly matched layer boundary conditions (10,11). For a periodic shell NW with a finite pitch,
we divided the NW into small segments with lengths of 50 nm along the NW axis and calculated the absorption cross section at each segment (Figure 3.4 and Appendix 17). In the periodic shell NW simulations, calculations were performed with a spatial resolution of $10/\sqrt{3}$, 10, and 10 nm for each axis and a calculation domain size of $1.6/\sqrt{3} \times 6 \times 0.9 \, \mu m^3$.

Appendix 5 References

Appendix 6

Figure A6.1 Annealed 100 nm Si cores. SEM images of a 100 nm Si core NW that was annealed at 775°C for 2 hours at ~ 0.3 Torr in hydrogen directly following core growth. Scale bars, 200 nm. We observe minimal rearrangement of 100 nm NW cores for times much longer (e.g. 2 hours) than periodic shell growth times (e.g. < 10 minutes), suggesting that traditional Plateau-Rayleigh instability does not drive rearrangement of the NW cores before or during growth of periodic shells.
Figure A7.1 Yield of diameter-modulated NWs. (A) Left, SEM image of a ~300 x 250 μm² area from a periodic shell NW growth substrate. The NWs were obtained from a synthesis in which Si
**Figure A7.1, Continued:** shells were deposited onto 100 nm cores at 775°C with a SiH₄ flow rate/partial pressure of 3 sccm/15 mTorr at a total pressure of ~0.3 Torr for 3 minutes. Scale bar, 100 μm. Right, high resolution SEM images of the single NWs denoted in the wide area image to the left. The red stars indicate representative images of NWs that clearly have diameter modulations; the blue indicates a NW without clear diameter modulation from SEM imaging. Scale bars, 1 μm. Examining all of the NWs in the large area region indicates that the yield of diameter-modulated NWs is ~90%. (B) Optical dark field image of a periodic shell NW growth substrate. The image was recorded using a 20x objective and an extra 1.6x magnifying lens; subsequently, the color tone of the entire image was adjusted in Adobe Photoshop to reduce the background in order to provide the best contrast for the diameter-modulation of the NWs to be visible.
Appendix 8

Figure A8.1 Periodic shell growth following removal of Au catalyst. SEM image of a representative Si periodic shell NW grown on a Si NW core whose Au catalyst was removed by a previously published procedure (1) prior to P-R crystal growth. Briefly, immediately after the growth of 100 nm Si cores, the growth substrate was removed from the reactor and immersed in KI/I₂ solution for 2 minutes, followed by rinsing with deionized water, etching in buffered hydrofluoric acid (BHF) for 1 minute and rinsing in deionized water. Before drying, the substrate was immersed in liquid N₂ and placed into the reactor; the pressure was immediately lowered to ~0.1 torr. The subsequent sublimation process prevents the collapse of NW cores via capillary action onto the growth substrate. When the reactor achieved base pressure, the temperature was increased to 775°C, followed by deposition of periodic shells under representative growth conditions; shells were grown for 3 minutes with a SiH₄ flow rate/partial pressure of 3 sccm/15 mTorr at a total pressure of ~0.3 Torr. Scale bar, 500 nm. Observed pitches of ~3-4 μm, inner diameters of ~300-400 nm, and outer diameters of ~400-500 nm are comparable to NWs whose periodic shells were grown under the same conditions directly after core synthesis without removal of the Au catalyst (see Appendix 12). The lack of significant difference between shells grown on NWs with or without Au indicates that Au does not contribute to the formation of periodic shells.

Appendix 8 References

Appendix 9

**Figure A9.1** Crystallographic characterization of Si periodic shell NWs in the [110] zone axis. (A,B) Bright (A) and dark (B) field TEM images of a NW tilted to the [110] zone axis. Scale bar, 500 nm. The dark field TEM image was recorded using a (2-20) reflected beam. Inset, selected area electron diffraction patterns in the [110] zone axis. The alternating dark-light lines along the length of the NW stem from thickness fringes due to the thickness change between the inner and outer shells.
Figure A10.1 Elemental mapping of a Si periodic shell NW. (A) A low magnification HAADF-STEM image of a typical periodic shell NW. Scale bar, 500 nm. (B) EDS maps of Si, C, O, and Au from the same area shown in (A). X-ray counts from Si and C match the locations of the NW and the amorphous carbon film, respectively, whereas O and Au counts are comparable to background signal. Elemental analysis suggests that impurities do not contribute to periodic shell formation.
Figure A11.1 Time-sequence of periodic shell growth. SEM images of NWs obtained from distinct syntheses for which Si shells were deposited onto 100 nm diameter cores at 800°C with a SiH$_4$ flow rate/partial pressure of 0.8 sccm/4 mTorr at a total pressure of ~0.3 Torr for 0 (left), 6 (middle), and 8 (right) minutes. Scale bars, 1 μm. The inner shell diameters of the NWs in the middle and right images are 160 nm and 240 nm, respectively; the outer shell diameters of the NWs in the middle and right images are 320 and 415 nm, respectively. The pitch of both NWs is ~4.5 μm, demonstrating that pitch does not change with time.
Figure A12.1 Pitch as a function of SiH$_4$ flow rate. Plan view SEM images of periodic shells grown on 100 nm cores at ~0.3 Torr total pressure and 775°C with (A) 0.3 sccm/1 mTorr, (B) 1 sccm/5 mTorr, (C) 3 sccm/15 mTorr, and (D) 9 sccm/47 mTorr SiH$_4$. Scale bars, 1 µm. These are representative NWs whose pitches contributed to the data shown in Figure 3.2A. Average pitches for (A), (B), (C), and (D) are 7.8, 3.8, 2.5, and 1.2 µm, respectively. Pitch is inversely proportional to SiH$_4$ flow rate. The diagonal lines in (D) are an artifact stemming from line scans of the SEM.
Figure A13.1 Pitch as a function of temperature. Plan view SEM images of periodic shells grown on 100 nm cores at ~0.3 Torr total pressure with 3 sccm/15 mTorr SiH₄ at (A) 735, (B) 775, (C) 815, and (D) 855°C. Scale bars, 2 µm. These are representative NWs whose pitches contributed to the data shown in Figure 3.2B. Average pitches for (A), (B), (C), and (D) are 1.2, 2.5, 4.0, and 8.3 µm, respectively. Pitch is proportional to periodic shell growth temperature.
Appendix 14

Figure A14.1 Pitch as a function of phosphine flow rate. Plan view SEM images of n-type periodic shells grown with (A) 0.75 sccm/4 μTorr and (B) 7.5 sccm/40 μTorr PH₃. All NWs were grown at ~0.3 Torr total pressure at 775°C with SiH₄ flow rate/partial pressure of 3 sccm/15 mTorr on 100 nm cores. Scale bars, 500 nm. The pitch was found to decrease with low flow of PH₃ and periodic shells were not observed for high flow rates of PH₃.
Figure A15.1 Surface area ratio comparisons with different shell volumes. (A) Ratio of the surface area (SA) of a periodic shell NW to the surface area of a straight NW as a function of...
**Figure A15.1, Continued:** outer diameter ($D_{outer}$) for different shell volumes added to a 100 nm core with fixed pitch of 3 µm. (B) The ratio of the minimum surface area of a periodic shell NW to the surface area of a straight NW as a function of pitch for different shell volumes added to a 100 nm core. For both plots, the volumes added to the periodic shell NWs and the straight NWs are equivalent for a given curve and inner diameters ($D_{inner}$) are fixed at 100 nm. Input volumes were derived from periodic shell NWs with inner shell lengths ($L_{inner}$) of 1500 nm, outer shell lengths ($L_{outer}$) of 1500 nm, $D_{inner} = 100$ nm, and variable $D_{outer} = 150, 200, 250, 300, 350,$ and 400 nm corresponding to the black, red, green, blue, cyan, and magenta curves. For reference, the blue curve in (B) is the same as that shown in Figure 3.2C. Absolute surface area values, as shown on the right axis in Figure 3.2C, are different for each plot trace, and thus specific surface areas were excluded from this multi-trace plot. (C) Ratio of the surface energies (SE) of experimentally-observed cross section periodic shell NWs to the surface energy of experimentally-observed cross section uniform NWs as a function of outer diameter ($D_{outer}$) for the same shell volumes added to a 100 nm core as in the dark blue curve in (A) with fixed pitch of 3 µm. Aspect ratios for both periodic and uniform NWs are 1 : 1.45 (red curve), 1 : 2 (green curve), and 1: 3 (black curve). For reference, the blue curve in (C) is the same as that shown in (A). In general, these plots show (1) that the surface area of a periodic shell NW can be lower than that of a straight NW of equivalent volume for a range of shell volumes, and (2) that longer pitches yield lower surface areas than shorter pitches for NWs with equivalent volume. Incorporation of the specific geometry we observe for Si periodic shells and the surface energy densities of the prominent facets of Si periodic shell NWs also yields lower surface energies compared to uniform diameter NWs with equivalent volume and cross section.
Appendix 16

Figure A16.1 Formation of high aspect ratio periodic shell NWs. Cross-sectional schematics of low (left) and high (right) aspect ratio Si periodic shell NWs. The NWs are capped by two Si(111) surfaces, four Si(113) surfaces, and two narrow Si(110) surfaces. It has been observed at conditions similar to our periodic shell growth conditions that interfacet mass-transfer of Si (i.e. net adatom surface diffusion from one facet to another) can occur provided that the diffusion lengths are much longer than the lengths of the facets (1,2). Specifically, net adatom diffusion from Si(111) to the Si(113) facet occurs, elongating the (111) surface (1-3). Hence, it is reasonable to assert that growth at lower SiH₄ partial pressures, which will yield longer diffusion lengths (3), \( \Lambda \), will result in higher aspect ratio structures with longer (111) surfaces due to net interfacet diffusion of Si adatoms from (111) to (113).

Appendix 16 References

Appendix 17

Figure A17.1 Light absorption in periodic shell NWs with short pitches. (A) FDTD simulations of the total light absorption in Si periodic shell NWs with outer diameter of 260 nm, and inner diameter of 205 nm with pitches of 400 nm (red) and 440 nm (green). Inner and outer shell diameters are the same as in Figure 3.4A and C. (B,C) Grating mode absorption profiles from FDTD simulations corresponding to peaks in (A) at wavelengths >700 nm. (B) Absorption mode profiles from green peaks located at 782 nm (left) and 929 nm (right) for the periodic shell NW with a pitch of 440 nm. Scale bars, 200 nm. (C) Absorption mode profiles from red peaks located at 755 nm (left) and 892 nm (right) for the periodic shell NW with pitch of 400 nm. Scale bars, 200 nm. The wavelengths of grating absorption modes are determined by the pitch of periodic shell NWs. For fixed outer and inner diameters, coupled grating modes can emerge at longer optical wavelengths when the pitch is reduced to the submicron regime.
Appendix 18

Experimental for Chapter 4

Nanowire synthesis

Silicon NWs were synthesized using a gold (Au) nanoparticle-catalyzed vapor-liquid-solid (VLS) process described previously (1). Briefly, 10, 30 and 80 nm diameter Au nanoparticles (15703, 15706 and 15710, Ted Pella, Redding, CA) were dispersed on the SiO$_2$ surface of Si growth substrates (600 nm thermal SiO$_2$, Nova Electronic Materials, Flower Mound, TX). NW growth was carried out at 450–460 °C at a total pressure of 40 Torr with silane (SiH$_4$, 99.9999%, Voltaix, Branchburg, NJ) as the silicon reactant, diborane (B$_2$H$_6$, 100 p.p.m. in H$_2$, Voltaix, Branchburg, NJ) as the p-type dopant, phosphine (PH$_3$, 1,000 p.p.m. in H$_2$, Voltaix, Branchburg, NJ) as the n-type dopant, and hydrogen (H$_2$, 99.999%; Matheson, Basking Ridge, NJ) as the carrier gas. Both p-type and n-type NWs were used for NW assembly and device fabrication in this work. For p-type NW growth, the flow rates of SiH$_4$, B$_2$H$_6$ and H$_2$ were 2.5, 3 and 60 standard cubic centimeters per minute (sccm), respectively. For n-type NW growth, the flow rates of SiH$_4$, PH$_3$ and H$_2$ were 1, 1 and 60 sccm, respectively. Typical growth times of 1–2 h yielded NWs with lengths of 40–80 µm. Cadmium sulfide (CdS) NWs were grown using Au nanoparticle catalyzed growth, with nanoparticles dispersed as above and CdS powder (99.999%, Alfa Aesar, Ward Hill, MA) evaporated in the high temperature zone and NWs obtained in the downstream lower temperature growth zone. Specific CdS NW growth conditions were CdS evaporation temperature, 675°C, growth zone temperature, 600°C, H$_2$ carrier gas flow rate, 20 sccm, pressure, 2.7 mTorr, and growth time, 60 min.
Shape controlled assembly

A range of target substrates were used in our studies, including Si wafers (Nova Electronic Materials, Flower Mound, TX) with SiO$_2$, Si$_3$N$_4$, Au, nickel (Ni) and SU-8 polymer (SU-8 2000.5, Microchem, Inc., Westborough, MA) surface layers. The substrate surface layer was cleaned by rinsing in isopropanol (IPA, Cleanroom® MB, KMG Electronic Chemicals, Inc., Houston, TX) for 30 s followed by nitrogen drying. S1805 (Microchem, Westborough, MA) for photolithography or polymethyl methacrylate (PMMA, 950-C2, Microchem, Westborough, MA) for electron beam lithography (EBL) was spin-coated, and photolithography or EBL was used to define arrays of trenches with shapes and widths as described in the main text. No additional surface modification followed exposure and development of these patterns.

Shape-controlled assembly of NW samples was carried out in a manner similar to shear-printing described elsewhere (1-3). Briefly a target substrate patterned with an array of trenches was mounted onto a micromanipulator-controlled moveable stage, covered with mineral oil (330760, viscosity, $v$, $\approx$ 70 mPa•s, Sigma-Aldrich, St. Louis, MO), and then the NW growth substrate was brought into contact with the target substrate with controlled contact pressure (values in text). The target substrate was moved at a constant velocity of $\sim$5 mm min$^{-1}$ with respect to the fixed NW growth substrate, and then the growth substrate was removed and the target substrate rinsed with octane (98%, Sigma-Aldrich, St. Louis, MO) to remove the lubricant. The minimum radius of NW curvature achievable by this process was determined by using ca. 200 nm radius of curvature trenches for 80 and 30 nm diameter silicon NWs, and 151.9 +/- 1.1 nm (mean +/- standard deviation) diameter Au nanoparticles (15712, Ted Pella, Redding, CA; size statistics obtained from the vendor’s characterization of 100 particles with transmission electron microscopy) for 10 nm diameter silicon NWs. Shape-controlled assembly of CdS NWs
was carried out in a manner similar to that for Si NWs. Tangent U-shaped and straight NWs were assembled by combing straight NWs as described previously (1) followed by assembly of U-shaped NWs.

**TEM sample preparation and characterization**

Arrays of U-shaped silicon NWs with different radii of curvature were prepared for transmission electron microscopy (TEM) characterization by fixing the arms of the assembled wires between Au metal layers while leaving the suspended NW tips exposed for imaging (Appendix 19). We introduced Au layers on both top and bottom of patterned PMMA for assembly as follows. (1) A Ni sacrificial layer (100 nm) was deposited on an oxidized silicon substrate by thermal evaporation (TE). (2) A square mesh gold ribbon network (100 nm) was defined on the Ni layer by EBL and TE. (3) Arrays of U-shaped 80 nm diameter silicon NWs were patterned as described above such that the straight arms and U-tips were on top of the gold mesh and open areas, respectively. (4) PMMA under the straight arms of U-shaped NWs was cross-linked by EBL using a dose of ~8,000 µC/cm$^2$. (5) A second Au mesh (100 nm thick) which was coincident in the x-y plane with the bottom mesh was defined on top of the cross-linked PMMA and deposited via TE. (6) The nickel sacrificial layer was etched in nickel etchant (TFB, Transene Company, Inc., Danvers, MA) for 1 h and then the free-standing arrays of U-shaped silicon NWs embedded in the Au-mesh/PMMA/Au-mesh trilayer were transferred to a copper TEM grid (300 mesh Cu, Ted Pella, Redding, CA). TEM characterization (JEOL 2100, JEOL Ltd. or aberration-corrected Zeiss Libra MC TEM, Carl Zeiss AG) was carried out at a beam accelerating voltage of 200 kV. Fourier-filtered images processed from the high-resolution TEM (HRTEM) images were used to characterize dislocations in the bent NWs.
Strain release tests

Arrays of suspended U-shaped silicon NWs were transferred to TEM grids as described above and introduced into a focused ion beam (FIB) instrument (dual ion/electron beam Zeiss NVision 40, Carl Zeiss AG). The FIB was used to cut one of the two suspended arms of a U-shaped NW (Ga$^+$ ions, 30 kV) while monitoring the NW release process in situ by SEM video-rate imaging (8 frames per second).

Raman spectroscopy characterization

Arrays of suspended U-shaped silicon NWs with some NWs cut by FIB were transferred to a glass slide. Raman spectra were acquired with a LabRam Evolution Multiline Raman Spectrometer (Horiba, Kyoto, Japan) equipped with 1800 blaze/mm grating and a 100x microscope objective lens with numerical aperture (N.A.) of 0.95. A continuous-wave (CW) diode laser with a wavelength of 633 nm was used as incident light source and circularly polarized using a zero-order quarter waveplate optimized for 633 nm. The laser power was ~26 µW and the laser spot size was ~1.5 µm in diameter.

Finite element simulations of NW bending

A geometrically nonlinear finite element model was used to simulate the large deformations of NWs under load. The modeling and simulations were carried out with commercial ANSYS 14.5 software. In our model, the NW is considered as a linearly elastic cantilever beam with elastic modulus of 188 GPa and Poisson ratio of 0.3 characteristic of silicon (4). The length and diameter of the cantilever beam are 20 µm and 80 nm, respectively. The in-plane shear forces generated during the experimental assembly process are expected to produce approximately
uniform distributed bending loads, which are applied in the simulations; these uniform bending loads ranged from 0 to 20 nN/μm. The deformation of the NW under different loading is shown in Appendix 20, Figure A20.1B. The corresponding load-dependent radii of curvature at the fixed end were calculated from the simulated results and are plotted in Appendix 20, Figure A20.1C.

NW waveguide experiments

Assembled U-shaped CdS NWs (diameters ~150 nm) on a SiO\textsubscript{2} substrate were used for optical waveguide experiments. The radii of curvature of U-shaped CdS NWs were 2 and 4 μm for the single NW waveguide and for the coupled waveguide system, respectively. A CW 405 nm diode laser (LRD-0405, LaserGlow Technologies, Toronto, Ontario) was used to excite the NWs, and wide-field photoluminescence images were collected through a 20x microscope objective lens with N.A. 0.50. The incident power of the pump laser was ~40 μW and the laser spot size was ~1 μm in diameter.

FDTD calculations

FDTD simulations were performed as reported previously (5). In the FDTD simulations with 150 nm diameter CdS NWs on a SiO\textsubscript{2} substrate, the refractive indices of CdS NWs (6) and SiO\textsubscript{2} were set to 2.7 and 1.5, respectively. To calculate the dispersion curve for the fundamental waveguide mode in an infinitely long single CdS NW (Appendix 21), a periodic boundary condition was defined along the long axis of the NW (y-direction) and perfectly matched layers were introduced at the other boundaries of the calculation domain with a size of 1.00 x 0.80 μm\textsuperscript{2} and a spatial resolution of 5 nm. Transmitted powers and coupling efficiencies were calculated using full 3-D FDTD simulations with spatial resolutions of 20 nm (Figure 4.4 and Appendix 22).
Calculation domains for the single U-shaped CdS NW and the tangent coupled straight and U-shaped CdS NWs were 9.00 x 15.50 x 0.75 µm$^3$ and 22.00 x 16.80 x 0.75 µm$^3$, respectively.

Appendix 18 References

Appendix 19

Figure A19.1 TEM of U-shaped NWs. (A) Schematics highlighting the structure of the free-standing U-shaped silicon NW arrays with arms embedded in Au mesh layers. (B) Dark-field optical image of U-shaped silicon NW array fixed and encapsulated in a double-layered gold mesh network transferred to a copper TEM grid. Scale bar, 50 μm. (C-E), Fourier-filtered high resolution TEM images of the tips of assembled U-shaped NWs (NW diameters all 80 nm) with radii of curvature of 3.0, 1.5, and 0.8 μm in (C), (D), and (E), respectively. Red arrows indicate dislocations. Scale bars, 5 nm. Insets, low magnification TEM images of the U-shaped, suspended NWs. Inset scale bars are 4, 2 and 2 μm in (C), (D), and (E), respectively. TEM analysis indicates that the overall defect density in the curved portions of the NWs increases as the radius of curvature decreases.
Appendix 20

Figure A20.1 Mechanism of NW bending. (A) Representative SEM images of 80 nm diameter silicon NWs assembled with normal pressures of (i) 0.8, (ii) 4.8 and (iii) 7.2 N cm\(^{-2}\). Scale bars all 1 \(\mu\)m. (B) Simulation of the deformation of the NW under bending loads 0 to 20 nN/\(\mu\)m. (C) The corresponding radius of curvature at the fixed end calculated from the simulation results in (B). These results are consistent with increasing shear force as the contact pressure is increased; that is, we find decreases in NW radius of curvature with increasing bending loads (simulation, (B)) or transfer normal pressures (experiments, (A)).
Figure A21.1 Optical properties of U-shaped CdS NWs. (A) Calculated dispersion curve of the fundamental waveguide mode (blue colored dots) in an infinitely long single CdS NW with a diameter of 150 nm on a SiO$_2$ substrate. Gray and blue lines in the graph denote the light line of SiO$_2$ and the spectral emission range of CdS, respectively. Only the fundamental waveguide mode is supported at the CdS emission wavelength (~515 nm) in this 150 nm
Figure A21.1, Continued: diameter NW. (B) Electric field ($E_z$, top) and intensity profiles ($E^2$, bottom) of the fundamental waveguide mode in the NW. Scale bar, 200 nm. (C) (i) Schematic of a single U-shaped CdS NW optical waveguide. When the NW is excited at the end of one arm, the resulting photoluminescence is coupled to an optical mode propagating along the NW axis (red arrows) and is then emitted at the end of the other arm of the NW. (ii) Calculated electric field intensity distribution of the single U-shaped CdS NW optical waveguide on a SiO$_2$ substrate. The NW diameter and radius of curvature are 150 nm and 2 µm, respectively. Scale bar, 2 µm. (iii) Measured photoluminescence image of a single U-shaped CdS NW waveguide with the same geometry as the simulations presented in (ii). The red and yellow arrows indicate the positions at which the NW was excited and propagating light was collected, respectively. Scale bar, 8 µm. The experimental observations (iii) are in agreement with the simulations (ii).
Appendix 22

Figure A22.1 NW photonic coupler. (A) SEM images of deterministically assembled straight and U-shaped NWs with controlled gap sizes of (i) 70 nm and (ii) 140 nm, respectively. Scale bars, 1 µm. Two step assembly (Appendix 18) was used to assemble the two-NW coupler. Silicon NWs were used in these assembly studies due to the much greater uniformity in diameter and length (vs. CdS NWs). (B) Calculated efficiencies of direct transmission through the optically pumped U-shaped NW (red) and crossover coupling to the tangent NW (blue) as a function of the gap size between U-shaped and tangent-straight CdS NWs. Location of excitation is at the end of one arm in the U-shaped NW. In the simulations, the diameters of both NWs and
**Figure A22.1, Continued:** the radius of curvature of the U-shaped segment are set to 150 nm and 4 µm, respectively. The coupling efficiency was calculated from transmitted powers along the NWs before and after the light coupling region. These results indicate that direct transmission and crossover coupling efficiencies can be adjusted by adjusting assembly parameters to rationally tune the gap between tangent NWs as demonstrated in (A).
Appendix 23

Description of Supplementary Video 1. SEM video recordings of the release process of a U-shaped Si NW. The radius of curvature of the U-shaped NW (NW diameter 80 nm) assembled on a copper TEM grid is 1.5 µm before cutting one arm with a focused ion beam (FIB). After cutting the upper arm (green arrow), the NW springs back to an almost straight configuration, suggesting that much of the strain introduced into the NWs during U-shaped assembly is elastic.
Appendix 24

Experimental for Chapter 5

Germanium (Ge) Nanowire (NW) Synthesis

Ge NWs were synthesized following a metal nanoparticle (NP)-catalyzed method reported previously (1). 30 or 100 nm diameter gold (Au) NPs (#15706 and #15711; Ted Pella, Redding, CA) were dispersed on SiO$_2$-coated Si wafers (p-type Si, 0.005 Ω cm, 600 nm oxide; Nova Electronic Materials, Flower Mound, TX) functionalized with 0.1% w/v poly-L-lysine (#P8920; 150,000 – 300,000 g/mol; Sigma Aldrich, St. Louis, MO) in water. The substrates were rinsed in deionized water, blown dry with nitrogen, and placed into a home-built chemical vapor deposition hot-wall quartz tube reactor with base pressure of ~3 mTorr. Ge NWs were grown via the Au NP-catalyzed growth mechanism for 2.5 hours at 270°C and a total pressure of 450 Torr and flow rates of 20 standard cubic centimeter per second (sccm) germane (GeH$_4$; 10% in H$_2$; Voltaix, Branchburg, NJ) and 134 sccm hydrogen (H$_2$; 99.999%; Matheson, Basking Ridge, NJ). For n-type doped Ge NWs, phosphine (PH$_3$; 1000 p.p.m. in H$_2$; Voltaix, Branchburg, NJ) was introduced during NW growth at a flow rate of 10 sccm.

Fabrication of U-trenches

Au was chosen as receiving substrate material for PL experiments because it has reflectivity of >98% for wavelengths longer than 900 nm. Au substrates with U-shaped trenches were fabricated by first thermally evaporating 50/1100/20/250 nm Cr/Au/Cr/Au on a SiO$_2$-coated Si wafer (p-type Si, 0.005 Ω cm, 600 nm oxide; Nova Electronic Materials, Flower Mound, TX). Next, UV photolithography was used to define U-shaped trenches in photoresist
(Microposit Shipley S1805; MicroChem Inc., Westborough, MA). The Si/SiO₂/Cr/Au/Cr/Au substrates were subsequently submersed in Au etchant (KI/I₂ solution; KI : I₂ : H₂O = 4 g : 1 g : 40 ml) for 24 seconds, rinsed twice in deionized water, submersed in Cr etchant (Chromium Etchant 1020; Transene Company, Inc., Danvers, MA) for 30 seconds, rinsed twice in fresh deionized water, and blown dry with nitrogen. Remaining photoresist was then removed via flood UV exposure, development in CD-26 (MF CD-26 Developer; MicroChem Inc., Westborough, MA) for 2 min, and finally by cleaning in a UV/ozone plasma at 200°C for 30 minutes. The clean Au U-trench substrates were then used for curved NW assembly. U-trenches defined by photoresist were fabricated by a similar method; photoresist layers (LOR 1A followed by Microposit Shipley S1805 diluted 1:1 with Microposit Thinner P; all from MicroChem Inc., Westborough, MA) were spin-coated on a SiO₂-coated Si wafer. Photoresist U-shaped trenches were then defined by UV photolithography as described above and the substrates were used directly for NW assembly.

**U-shaped NW Assembly**

U-shaped Ge NWs were assembled by a shear transfer technique (2, 3). Mineral oil (#330760, viscosity n ≈ 70 mPa·s; Sigma-Aldrich, St. Louis, MO) was dispersed on the Au U-trench receiving substrate to serve as a lubricant during shear transfer. The NW growth substrate was then placed on the receiving substrate with pressure ~5 N/cm² and translated over the receiving substrate at ~1 cm/min. Next, mineral oil was removed by rinsing in octane (98%; Sigma-Aldrich, St. Louis, MO). Finally, the substrate was cleaned in an oxygen plasma with power 50 W for 1 minute.

**Electron Microscopy**
Scanning electron microscope (SEM) images were recorded on a Zeiss (Oberkochen, Germany) Ultra Plus field emission SEM. Transmission electron microscope (TEM) images and selected area electron diffraction patterns were recorded with a JEOL (Tokyo, Japan) 2100 TEM operating at 200 kV accelerating voltage.

**Near Infrared (NIR) Photoluminescence (PL) Imaging and Spectroscopy**

High-magnification NIR PL microscopic imaging of U-shaped Ge NWs was performed in a home-built hyperspectral microscopic imaging setup which afforded both wide-field imaging and single-point PL emission spectroscopy (Appendix 25). A 658 nm laser diode (Thorlabs, Inc., Newton, NJ) with a 40 μm diameter spot focused by a 100x objective lens (high transmission with anti-reflection coating in the infrared; numerical aperture, N.A. = 0.80; Olympus Corp., Tokyo, Japan) on the sample plane provided excitation. The spot size was tuned by changing the distance between the collimating lenses L1’ and L2’. The excitation light was passed through a 750 nm shortpass filter (Omega Optical, Inc., Brattleboro, VT) and circularly polarized to minimize anisotropy in intensity with respect to the anisotropic NW geometry (4). The excitation power on the sample plane was 80 mW, giving an average power density of 6.4 kW/cm² over a spot size 40 μm in diameter. The resulting NIR PL passed through an 1,100 nm longpass filter and was collected with exposure time 1 s using a liquid-nitrogen-cooled two-dimensional (2D) InGaAs camera (Princeton Instruments, Trenton, NJ) with high quantum efficiency up to 1,700 nm. Thus, NIR PL images showed contributions from the range 1,100-1,700 nm; a one-dimensional InGaAs array detector with sensitivity from 1,100-2,100 nm was used for spectroscopy (please see below).
The NIR PL image was flat-field corrected by automatically dividing the raw 2D matrix data by the laser excitation intensity profile, which was obtained by taking an autofluorescence image of a clean silicon wafer under the same imaging settings. To take a white-light illuminated, bright-field image of the same field of view as the microscopic NIR PL image, the 658 nm laser excitation was replaced by a halogen lamp (Dolan-Jenner, Boxborough, MA) placed before the offset lens L3’. Bright field optical images were recorded in the reflection mode using the same emission filter with an exposure of 1 ms but not flat-field corrected. The sample was mounted on a three-dimensional translational stage (Newport Corporation, Irvine, CA) in the inverted mode, allowing for position control for image acquisition. All NIR fluorescence images were plotted using the Matlab software under the ‘hot’ colormap.

NIR micro-PL (µ-PL) spectroscopy was performed using the same 658 nm laser excitation, but focused to a much smaller spot (diameter ~1 µm) than the wide-field imaging by removing the collimating lenses L1’ and L2’ as well as the offset lens L3’ from the optical path and inserting an iris to further confine the size of the excitation beam on the sample plane. The measured total power on the sample plane was 1.3 mW, covering a circular spot with a measured diameter of ~1 µm on the front focal plane of the 100x objective lens, yielding a power density of ~166 kW/cm². The emitted PL was filtered with the same 1,100 nm longpass filter and directed into a triple turret spectrometer (Acton SP2300i; Princeton Instruments, Trenton, NJ). The spectrometer was equipped with a liquid-nitrogen-cooled InGaAs linear array detector (Princeton Instruments, Trenton, NJ) with high quantum efficiency up to 2,100 nm. The spectrum for each spot was taken in the range of 1,100-2,100 nm with an exposure time of 300 ms; the number of acquisition iterations is specified in the figure caption for each corresponding spectrum. All raw spectra were corrected to remove the higher-order laser diffraction peaks and
to account for the wavelength-dependent sensitivity profile of the detector as well as the wavelength-dependent extinction profile of the emission filter.

**Raman Spectroscopy**

Micro-Raman spectra were recorded from NWs assembled in photoresist U-shaped trenches using a Horiba (Kyoto, Japan) LabRAM Evolution confocal microscope equipped with an 633 nm excitation laser, 1800 blaze mm\(^{-1}\) grating, Synapse CCD detector, and a 100x (NA = 0.95) objective lens. The incident laser was circularly polarized to avoid any influence of the anisotropy of the curved portion of the NW on the Raman spectra (5-7). Incident laser power was maintained at 26 µW to preclude laser heating of the NWs (8). Typical integration times for spectra were ~10 minutes per point; this duration was divided into ~10 acquisitions to minimize the contribution of noise. Spectra were best-fitted using a least-squares method to combinations of Gaussian and Lorentzian curves using the Horiba LabSPEC software which accompanied the microscope.

**Strain determination in curved NWs**

Geometric calculations were applied to approximate the tensile strain in curved Ge NWs in accordance with previous work (6,9-12). The geometry is shown schematically in Appendix 27. In brief, we approximate the length of a NW with diameter D before and following bending to radius of curvature \(\rho\). At distance \(rD\) from the inner edge, where \(r\) is an index with \(0 < r < 1\) representing the relative position between inner and outer radius of the NW, the NW length (assuming circular curvature) is expressed as \(L_r = \pi(\rho + rD)\).
The length of the curved NW at its center $(r = 0.5)$ was the length of the wire before bending (known as the neutral axis), or $L_{r=0.5} = \pi(\rho + 0.5D)$. Thus, strain at a given point throughout the wire is expressed as:

$$\varepsilon_r = \frac{L_r - L_{0.5}}{L_{0.5}} = \frac{\pi(\rho + rD) - \pi(\rho + 0.5D)}{\pi(\rho + 0.5D)} = \frac{D(r - 0.5)}{\rho + 0.5D}$$

For $\rho \gg D$, strain at the outer edge of the NW (where $r = 1$) is expressed as:

$$\varepsilon_{\text{tensile, outer edge}} = \frac{D}{2\rho}$$

Appendix 24 References

3. Chapter 4.
Appendix 25

Figure A25.1 Optical setup used for NIR PL imaging and spectroscopy of Ge NWs. In brief, non-polarized excitation light from a red diode source (LS) is filtered by an excitation filter F1 and focused via objective lens (OB) onto an Au substrate on which the Ge NWs have been assembled. The size of the excitation beam is controlled by the collimating lenses L1’ and L2’, the offset lens L3’ and the iris I. Emitted light is then routed via removable mirror (M4’) to either a 2D InGaAs array for PL imaging or a spectrometer (SP) and 1D InGaAs array for recording PL spectra. Please see Appendix 24 for more details. Optical element labels: 1D: 1D detector array; 2D: 2D camera; DC: dichroic mirror; F1: excitation filter; F2: emission filter; I: iris; L1 and L2: collimating lenses; L3: offset lens; L4: tube lens; L5: relay lens; L6: spectrometer lens; LS: laser diode; M1 and M2: relay mirrors; M3: objective mirror; M4: camera mirror; M5 and M6: horizontal periscope mirrors; M7 and M8: vertical periscope mirrors; MS: mechanical shutter; OB: objective; QW: quarter-wave plate; S: shutter (manual); SP: spectrometer; TR: three-dimensional translation stage; WL: white light source. Optical elements labeled with ‘ are mounted on flip mounts, allowing easy removal and insertion when switching between the NIR PL imaging, white-light bright-field microscopic imaging and NIR μ-PL spectroscopy.
Figure A26.1 PL emission centers versus $\rho$ for n-type phosphorous-doped Ge NWs with $D = 100$ nm. $N = 15$ NWs for the straight point and 3 NWs for the curved NW points; error bars denote ±1 standard deviation. Interestingly, the PL emission center for both n-type and intrinsic Ge NWs is approximately equal for the same $\rho$ and $D$. 

Figure A27.1 Schematic depicting strain distributions in a NW before (left) and following (right) U-shaped assembly. Red, green, and blue shading represent compressive, neutral, and tensile strain. Labels: CB: conduction band; D: NW diameter; ε: strain; E: band energy; ρ: radius of NW curvature; r: index representing the relative position between inner and outer radius of the NW; VB: valence band. The plots on the top right schematically depict the spatial distribution of strain (top) and band energies (bottom) from the inner (r = 0) to the outer (r = 1) edges of the curved NW. As a NW is curved, its inner (outer) edge experiences compressive (tensile) strain, yielding a wide-to-narrow band gap profile from inner to outer edge. Please see Chapter 5 and Appendix 24 for more details.
Figure A28.1 PL emission center vs. strain for NWs with different dopants and Ds. Intrinsic, n-type, and intrinsic Ge NWs with D = 100, 100, and 30 nm correspond to blue squares, black diamonds, and red circles, respectively. The green triangle denotes the most red shifted emission observed from a single NW. The red line shows a linear fit ($R^2 = 0.93$) of PL emission center $E = -0.062 \varepsilon + 0.82$ eV as a function of $\varepsilon_{\text{tensile}}$. The linear fit did not include points with $\varepsilon_{\text{tensile}} > 2.3\%$. N = 25 (15) intrinsic (n-type) Ge NWs for the $\varepsilon_{\text{tensile}} = 0$ point and 5 (3) intrinsic (n-type) Ge NWs for the curved NW points; error bars denote ±1 standard deviation. The PL emission center as a function of $\varepsilon_{\text{tensile}}$ – rather than as a function of trench geometry (e.g. $\rho$ and trench width) – is nearly identical; or conversely, the emission center is different for identical trench geometries for NWs with different Ds and thus strains. This observation helps to rule out the influence of the configuration of the substrate on the NIR emission from strained Ge NWs.
Figure A29.1 Crystallographic characterization of the Ge NWs. TEM image of a Ge NW with \( D = 100 \) nm. Scale bar, 100 nm. Inset, selected area electron diffraction pattern from the area of the NW shown in the image. Based on indexing the electron diffraction pattern to the \(<111>\) zone axis, the growth direction of the Ge NWs is \(<110>\); this growth direction matches that reported previously for similar Ge NW synthesis conditions (1).

Appendix 29 Reference