SYNTHESIS AND RAMAN SCATTERING STUDIES OF NOVEL SEMICONDUCTOR NANOSTRUCTURES: Si, Ge AND GaAs TWINS TWINNING SUPERLATTICE NANOWIRES

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Physics
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This thesis work focuses on synthesis of novel semiconductor nanostructures: nanowires, quantum dots and twinning superlattices by Pulsed Laser Vaporization (PLV) and Thermal Batch Process (TBP) and the studies of their optical properties. We have developed growth and synthesis routes to produce Ge and Si nanowires of diameters ranging from 3nm to 10nm that exhibit quantum confinement effects. The asymmetric Raman lineshape predicted for scattering from confined optical phonon by Richter, and the Fano interference lineshape in n-type Si and Ge are found to be similar. However, the physics of either phenomenon is distinctively different. We performed a series of Raman scattering experiments on Si and Ge nanowires to determine the true origin of the asymmetry. The experiments were conducted under two conditions: high wire density and low wire density, corresponding to poor thermal anchorage and good thermal anchorage on substrate. We identified three physical phenomena that contribute to the lineshape: Phonon confinement, photo-stimulated and thermally induced Fano scattering. We can distinguish each of these processes based on the diameter of the wire and the laser flux dependence of the scattering and the evolution of the lineshape at low laser power with nanowire diameter.

Which effect dominates depends on the contact of the Raman sample to the substrate, the substrate thermal properties, and the diameter of the nanowires. We have proposed a coupled phenomenological model which takes the phonon confinement and Fano processes into account that best describe the observed asymmetry in the phonon lineshapes. We are the first to report true phonon confinement in Si and Ge nanowires that shows the evolution of the lineshape asymmetry with diameter (3 nm to 30 nm) first predicted by Richter. We have also investigated the effect of oxide layer, and strain induced by the oxide layer on the first order Raman scattering from Si nanowires. Our data reveal that: a) one can either introduce strain or suppress strain depending on the dry oxidation route; in situ suppresses strain where as ex situ induces strain and b) the asymmetric lineshape in the phonon mode is affected by the strain and the thickness of the oxide layer.

Finally, we have used photoluminescence to demonstrate that twinning superlattice of GaAs nanowires of classical size $d \geq 30$nm can exhibit quantum confinement effects e.g., a red shift in the band gap (as predicted by theoretical investigations). In addition, Raman scattering spectrum from the GaAs twinning superlattice reveals a new strongly enhanced peak at 515 cm$^{-1}$ that is not observed in the bulk. We attribute this peak to an undetermined twinning.
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DEDICATION

To my dearest Wife and Son

The embodiment of my existence

To my Family

For being there with me throughout my entire education

To my Group

For the support over the course of my graduate education

To all I say

Me da mo ase.
Chapter 1

Semiconductor Nanowires

1.1 Introduction

The advent of the bipolar transistor in 1960 forever changed the nature of electronics. Prior to this, high power, large volume vacuum tubes were used as circuit elements. Silicon solid state devices mark the beginning of an electronic technological revolution. Most of the early semiconductor devices were fabricated from bulk crystalline material. But as the quest for rugged high performance and high speed devices developed, miniaturization became important and integrated devices built on large wafers emerged using lithography to pattern many devices per unit area. The progress in the last three decades can be characterized by a gradual displacement of these Si devices by thin epitaxial film and multilayered structures (two dimensional) with special properties. These structures have led to the development Field Effect transistors such as High Electron Mobility Transistors (HEMT) [1] and Metal Oxide Semiconductor Field Effect Transistors (MOSFET) [2], quantum well lasers [1,3], optical modulators [4,5], nipi-photosensitive elements [1,6-8], quantum well photodetectors [9], avalanche photodiodes[1,7,10] etc. In these quasi-two dimensional systems, most of the electronic and vibrational properties are different compared to that of the bulk crystal, mainly due to the so-called quantum size effects. The most dramatic changes in properties takes place in these quantum size structures where the carriers/phonons are confined in the region of a
characteristic size of the order of electron mean free path/phonon mean free path. The past decade has witnessed a revolution in the science and technology of one-dimensional systems: semiconductor nanowires and carbon nanotubes. These nanoscale, one-dimensional structures have stimulated great interest due to their importance in basic scientific research and potential technological applications [11,12]. Many unique and fascinating properties have been proposed and demonstrated for a class of materials such as metal-insulator transition [13], superior mechanical toughness [14], high luminescence efficiency [15,16], enhancement of thermoelectric figure of merit [17] and a low lasing threshold [18-20]. These one dimensional structures can also be used as the building blocks to assemble new generations of nanoscale electronic circuits and photonics [21-25].

The advances in the growth of one dimensional novel structure of semiconductors could be traced back to the 1960s where whiskers semiconductor growth and R&D was at its peak. Semiconductor whiskers such as Si [26,27], Ge [28,29], GaP [30-32], GaAs [27,33-39], InAs [39-41], etc., grown on a substrate in a Chemical Vapor Deposition system were widely and extensively investigated. The growth mechanism of these microstructures have been described in detail by Wagner and co-workers [26, 42, 43], Givargizov and Chernov [44] and Givargizov [27,44]. The diameter of the whiskers usually ranged from a few micron to tens of microns, due to the ~µ diameter of the metal liquid drop or micro cluster that initiates and sustain the whisker growth process. The minimum critical diameter of a stable liquid micro cluster is given by [45]

\[
d_{\text{min}} = \frac{4\sigma n_i V_i}{RT \ln \sigma}
\]

(1.1)
where $\sigma_{lv}$ is liquid vapor interfacial energy, $V_l$ is the liquid molar volume, $R = 8.314472 \text{ J mol}^{-1}\text{K}^{-1}$ is molar gas constant, $T$ is the absolute temperature and $\sigma$, the supersaturation of the vapor is defined as,

$$\sigma = \frac{p - p_o}{p_o},$$

(1.2)

where $p$ is the vapor pressure and $p_o$ is the equilibrium vapor pressure of the solid at temperature $T$. As the search for whiskers of only few nanometers in diameter began, this diameter restriction on the droplet led to alternate approaches such as “V-grooves”, electrochemical/chemical processes, and mesoporous channels in membranous template [46-51] to produce small metal particles that initiate nano-whisker (nanowire) growth. These approaches provided nanowires with diameters ranging from tens to hundreds of nanometers.

To observe electronic confinement effects in these novel structures require nanowires of few nanometers in diameter. In 1995, the use of Pulsed Laser Vaporization technique to synthesize singled-walled carbon nanotubes provided the ideas that it might also be useful for making semiconductor nanowires of few nanometers in diameter. Results were first achieved in 1998 by Morales and co-workers [52] and Zhang and coworkers [53]. Since then, semiconductor nanowire growth has blossomed. Shortly thereafter, a proliferation of semiconductor synthesis techniques for synthesizing elemental to ternary compound nanowires were achieved: Si [52-54], Ge [52,55,56], SiC [57,58], ZnO [59], GaAs [52,60-63], InP [62], GaP [62], GaN [25,62,64], CdTe [65], CdSe [65], AlGaAs [62] and superlattice nanowires: Si/GeSi [66], GaAs/GaP [67], GaAs/GaInAs [68] of typical diameter ranging between 10nm – 200nm.
1.2 The Synthesis Breakthrough

A number of synthesis techniques, such as pulsed laser vaporization (PLV) [21,22,53,56,62-64], chemical vapor deposition (CVD) [57,69], laser-assisted chemical vapor deposition (LA-CVD) [66], lithography [70-72], sublimation [73], thermal evaporation [74-76], thermal oxidation [77,78], chemical and electrochemical processes [79-82], nanochannel templates [83,84], etc., were developed to fabricate one dimensional novel structures of semiconductors. So far, PLV, CVD and LA-CVD are the most widely used synthesis techniques. These techniques provided some control over wire diameter and length that make them suitable to synthesize elemental nanowires, binary compound nanowires, ternary compound nanowires and nanowire superlattices. These synthesis processes are mostly governed by the Vapor-Liquid-Solid (VLS) growth mechanism. In the VLS growth mechanism, an alloy cluster of catalyst and the semiconductor is formed. These agglomerate till they reach critical sizes imposed on them by the experimental conditions. As the cluster absorbs more of the semiconductor in the vapor phase, it saturates. At supersaturation, the excess semiconductor precipitates to form the nanowire. Detail of this process is given in chapter two. Morales and co-workers [52] were the first to demonstrate the use of PLV to synthesize Si nanowires of 20nm average diameter via the Vapor-Liquid-Solid (VLS) mechanism by adding Au or Fe to the starting Si material.

In the same year Zhang and coworkers [53] used PLV oxide assisted growth mechanism to synthesize Si nanowires (i.e., no metal was used in the target). Other techniques, such as mechanical atomic force lithography [85], thermal oxidation [77], physical evaporation[74], ion beam [71], and electrochemical [80] were demonstrated for the synthesis of SiC [86], GaN, CdS, and Si, etc. 1999 saw a rapid growth in the synthesis, characterization and studies of the
fundamental properties such as photoluminescence. By 2000, almost 500 papers had been reported on synthesis, morphological characterization, optical properties (photoluminescence) and potential technological applications of semiconductor nanowires. The new millennium saw improvement in the synthesis techniques such as the use of in situ carrier gas heating, developed by our group to control and stabilize the target temperature in PLV system, the use of laser assisted-CVD techniques, as well as the development of sophisticated bottom-up approaches to assemble these nanowires for high density circuit applications. The range of nanowire materials that have now been synthesized span elemental, binary and ternary compounds and some simple superlattices. Apart from these nanowires, coaxial nanowires of SiC and Si$_3$N$_4$ sheathed with BN [87] have been synthesized recently. Most of these wires were synthesized by PLV, CVD or LA-CVD. Thus, these synthesis techniques have been shown to be quite robust and have opened up a new frontier in nanoscale materials.

The technological applications of the nanowires are of paramount importance to the industrial community. The most challenging issue is the assembly of these structures into high density configurations for particular device applications. Different existing techniques such as Photolithography, Scanning Probes Methods and Soft Lithography, and new ones, such as Bottom-Up Methods are being developed and modified to accomplish this goal.

1.3 **What special properties might be expected from Semiconductor Nanowire?**

One dimensional nanostructures of semiconductor materials of highly crystalline quality and a few nanometers in diameter (2-10nm) with high aspect ratio (> 100) (see *Figure 1–1* and *Figure 1–2*) provides a promising route for compact high-density nanoscale devices.
Figure 1–1: SEM image of tangled Si nanowires synthesized by PLV via the VLS growth mechanism. These wires were grown in our lab by the author. Typical diameter was 7nm and length exceeding 5µ were observed. Target was crystalline Si powder (45µ to 100µ in size) with 10% Fe (1µ-3µ in size)
Figure 1–2: HRTEM image of Si nanowire synthesized by the author. The \{111\} atomic planes exhibit 3.104nm spacing as compared to 3.10nm in the bulk. The \{111\} planes are perpendicular to the wire axis suggesting a \textless{111}\textgreater growth direction. The crystalline core has a diameter sheathed by Si oxide. Wires were grown from crystalline Si powder (40-50\(\mu\) in size) with Fe powder (1\(\mu\)-3\(\mu\) in size) target.

The high aspect ratio of these nanoscale structures allows the device to be interrogated electrically. At these small diameters that approach the physical lengths of the systems such as electron and phonon wavelengths, exciton radius, impurity orbit radius, electron screening length, electrostatic dipole interaction range, etc., quantum confinement effects can become dominant and the physical properties depart entirely from that of the crystalline bulk, even though there may be no change in the atomic arrangement. In strongly confined semiconductor nanowires, band gap may be direct, even though in the bulk band gap is indirect [88,89]. A correlation of band gap and diameter of the nanowires suggest possible tunability of the band gap energy of the semiconductor by changing the diameter. Decreasing diameter result in the increasing of the band gap energy [89]. From effective mass approximation calculations on spherical Si quantum dot, Efros and Efros [90] predicted a blue shift in the band gap energy, given the effective band gap energy, \(E_{\text{eff}}\) as:
$E_{\text{eff}} = E_g - E_{\text{ex}} + \frac{\hbar^2 \pi^2}{2 \mu d^2}$ \hfill (1.3)

where $\hbar$ is the Plank constant, $d$ is the diameter of the spherical quantum dot, $E_g$ is the band gap energy of the bulk. The exciton energy, $E_{\text{ex}}$ and the reduced mass $\mu$ are respectively given as:

$E_{\text{ex}} = \frac{E_b}{n^2}$ \hfill (1.4)

with

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

$E_b = \frac{\hbar^2}{2\mu a_B^2}$. \hfill (1.5)

$a_B$ is the excitonic Bohr radius and $E_b$ is the exciton binding energy. Since the work of Efros and Efros [90], enormous effort have been directed towards photo-emissive properties of semiconductor materials due to quantum confinement effects. Recently, Ranjan and coworkers [91] reported a modification of the effective band gap energy by the diameter inhomogeneity of the quantum nanocrystallites and proposed an effective exponent $\gamma_{\text{eff}}$, with a range $1.4 \leq \gamma_{\text{eff}} \geq 2$. This causes a modification of the effective band gap energy to:

$E_{\text{eff}} = E_g - E_{\text{ex}} + \frac{c'}{d^\gamma_{\text{eff}}}$ \hfill (1.6)

where $c'$ is an adjustable parameter.
1.3.1 Introduction to Electronic and Phonon Confinement Effect

For the past twenty five years, size quantization have been well studied in two dimensional systems such as thin films, metal-oxide-semiconductor structures, single heterojunctions, quantum wells, superlattices, etc [92]. Studies of quantum wells and superlattices have lead to the development of such devices as Field Effect transistors like the High Electron Mobility Transistors (HEMT) [1] and Metal-Oxide-Semiconductor Field Effect Transistors (MOSFET) [2], quantum-well lasers [1,3], optical modulators [4,5], nipi-photosensitive elements[1,6-8], quantum well photodetectors [9], avalanche photodiodes[1,7,10], etc. These systems all have a mixed discrete-continuum energy spectrum associated with a uni-directional confinement axis and a bi-directional energy continuum associated with other two dimensions. In a one-dimensional system, however, there is a lateral confinement in two-directions which can, for example, be used to tune physical properties, such as the band gap in some systems. For example, theoretical investigations of the optical properties of free standing quantum wires by Sanders and coworkers [88] predicted a direct band gap characteristic, for an indirect band gap semiconductor which is diameter dependent. This has been demonstrated in Si nanowires [93], where the authors showed a blue shift diameter dependence in the band gap. Also, it is known that Porous Si (PS) and some quantum dots (0-D systems)[15,94-96] are representative of the low dimensional systems that exhibit band gap and photoemission dependent on diameter. Though PS exhibit the dependence of the band gap on diameter (see Figure 1–3) in the whole range of wavelengths from infrared to the ultraviolet band [97], the physical origin of such characteristics is of debate. This is largely due to the heterogeneity of the PS resulting from the intricate mechanism of formation and complicated morphology. However,
the dependence of the photoemission on the diameter of a quantum dot has been demonstrated using CdSe quantum dots (see Figure 1–4).

Phonon confinement effects have been observed in semiconductor nanocrystalites, nanowires and disordered structures using Raman Spectroscopy [98-104]. Our group has recently criticized this interpretation in the case of Si [105] and Ge [106] nanowires. Phonon confinement in Si, for example is usually reported as a downshift in the bulk Lorentzian Raman band position and an asymmetric broadening of the lineshape to lower frequency. In small diameter nanowires, the phonons are laterally restricted, leading to the relaxation of the $q = 0$ Raman selection rule.

![Figure 1–3: Optical absorption spectra of porous Si film containing nanocrystalites of different average sizes. Smaller crystallites have higher band gap energy. The absorption edge, characteristic of the band gap as shown, is diameter dependent [89].](image-url)
Figure 1–4: On the left are six different vials containing CdSe quantum dots of different diameters exhibiting diameter dependence photo-emissive properties, when excited with a UV laser. On the right is HRTEM of 5nm CdSe quantum dot showing the atomic arrangement in the dot [95,96].
Figure 1–5: Generic, bulk phonon dispersion of Longitudinal optic (LO) and the Transverse Optic (TO), Longitudinal Acoustic (LA) and Transverse Acoustic (TA) branches in the particular direction in q space. Assuming the bulk has a Raman active mode at \( q = 0 \), the shaded region indicates the region of Raman activity associated with LO and TO phonon confinement in the wire of diameter \( d \). In this case, the confinement is in the direction perpendicular to the phonon wave vector \( q \) in the figure.

As we shall see later, confining a phonon of wave vector \( q_0 \) in a small nanowire of diameter \( d \) requires the superposition of many bulk phonons covering the range \( \Delta q = (q - q_0) \sim 1/d \). This result is essentially a manifestation of the uncertainty principle: i.e. \( \Delta q \sim 1/d \). This range of \( \Delta q \) of “activated” phonons should lead to a broadening and shifting of the nanowire phonon Raman band relative to the band symmetry in the bulk. However, the phonon mean free path should be larger than the wire diameter. This need not be the case in a real nanowire with larger numbers of
impurities or dislocations, or if anharmonic scattering is large. To quantitatively understand these changes in Raman activity, let us consider the generic phonon bands shown in Figure 1–5 associated with the bulk. Assuming both optical branches are Raman active at the zone center, two Lorentzian Raman lines would be observed for the bulk solid associated with the $q = 0$ phonons at A(LO) and B (TO), where LO and TO stand for Longitudinal and Transverse Optic phonons, respectively. This is the result of “$q = 0$” Raman selection rule in an infinite periodic system [99]. In a nanowire, with diameter $d$, this selection rule can be broken and the Raman activity spills into the Brillouin zone in the shaded region. For the generic LO mode shown in the Figure 1–5, the wire Raman band softens and asymmetrically broadens to lower frequency. In the case of the generic TO mode, the dispersion has an opposite sign and the nanowire band would be expected to upshift and asymmetrically broaden to higher frequency.

1.3.2 Nano-scale devices

Semiconductor nanowires are the nanoscale building blocks that could, through “bottom up” assembly and other techniques, enable diverse application in nanoelectronics and photonics [107]. Already, individual elemental, binary and ternary compounds have been used to fabricate field effect transistors, photodetectors, and bio/chemical sensors, while sophisticated light emitting diode, and logic devices have been realized by assembly of both n-and p-type doped semiconducting nanowires into crossed junctions [21,22,108,109]. Also ZnO nanowire lasers [23,24,110], field emitters from SiC and Si [86,111,112], and nanowire-based batteries [113] are some of the early candidates for the nanoscale devices. But the most crucial and challenging issue in many of the applications of these one dimensional novel structures is how to assemble
them into a desired array. This can be approached either via “self-assembly” or by direct assembly. The latter can be accomplished by growing oriented nanowires at specific locations on a substrate, or by assembly from nanowires in solution using electrophoretic forces [114,115].

1.3.2.1 Nanosensors

The performance of many commercially available sensors is limited by their dimensions which can limit the response time. Other issues that may be addressable at the nanoscale are the thermodynamic stability, operating temperature, sensitivity and selectivity. Semiconductor nanowire sensors that overcome most of the micro-scale limitations have been demonstrated. In 2001, Cui et al. [21] used a Boron-doped silicon nanowire to create a highly sensitive, selective, real-time electrically based sensor for biological and chemical species. By suitable surface modification, the nanowires were found to exhibit changes of electrical conductance to different substances adsorbed on the wire surface and could detect certain biomolecules down to the picomolar range at room temperature. This landmark result suggests that semiconductor nanowires with suitable surface modification might provide the sensitivity and the selectivity needed to detect a variety of molecules, atoms or ions at lower concentration and in real time.

1.3.2.2 Nanolasers

Using self-organized zinc oxide nanowires grown normal to the surface of a sapphire substrate via simple vapor transport and condensation process, Yang and co-workers fabricated and demonstrated a room temperature ultraviolet nanolaser [110]. These wide band-gap
nanowires form natural laser cavities with diameters varying from 20 nm to 150 nm and lengths up to tens of microns. Under optical excitation, lasing action was observed at 385 nm with an emission line width of less than 0.3 nm. However, it was found to be very difficult to excite the self-organized nanowire array with an electric current [110]. Recently Duan and co-workers used a crossed p-doped and n-doped Si nanowire junction to create a light emitting device (LED). When a positive voltage was applied to the p-doped nanowire, light was emitted from the junction; a process just like light emitting diodes. These nano-LEDs offer a range of possibility in the optoelectronic industry. A scale up of such technique can offer an extraordinary high resolution LED arrays.

1.3.2.3 Logic Circuits

Semiconductor nanowires have also been explored as the building blocks for high density circuits, i.e., field effect transistors (FET) [114,115], diodes [22,115] and complementary inverters [22]. Lieber and coworkers used microfluidic techniques to assemble the semiconductor nanowire diodes and transistor to form logic AND, OR, NOR and XOR gates that demonstrated basic logic computations [109]. This work is an important step towards the realization of “bottom up” construction of high density memories and computations using nanowires.

1.4 Advances in the assembly techniques of Semiconductor Nanowires

One of the most significant challenges facing the electronic industry is the assembly of many nanowire devices in a desired configuration on the chip. Conventional photolithography,
the backbone of the existing silicon technology, is a two step process: the making of the mask or master and the reproduction of replicas of the mask. The desired circuitry after design is reduced and converted onto an opaque metallic film like chromium or a transparent plate, like glass or silica in a form of patterns; this is the mask or the master. Photolithography is then used to reduce the patterns onto a wafer. A wafer coated with a photosensitive material or photo-resist (usually organic polymer) is placed under the mask. A UV light is shined on the mask and is then focused on the wafer by a lens. The photo-resist is selectively removed depending on the type, i.e., “positive” or “negative” to expose the wafer surface. Etching, evaporation and other techniques are used to create the final pattern on the wafer. This photolithographic technique which is used to manufacture microchips in the existing technological industry is limited in the size of the structure it can create, first, by the wavelength of the UV light (250 nm) i.e., \( d \sim \lambda \) currently used in the production processes, and, secondly, the wires have to be already assembled. These disadvantages have lead to research on non-conventional approaches that have not been explored in the traditional electronic industry approaches. Techniques such as soft lithography: nanofluidic-assisted-template assembly, macroscopic field force assisted assembly, i.e., the use of electric/magnetic field, and Scanning Probe manipulation of nanowires are being explored in the assembly processes. These techniques will be discussed in this section with emphasis on the progress in using such techniques, advantages, disadvantages and limitations.

### 1.4.1 Soft Lithography: nanofluidic assisted nanowires assembly

In the soft lithography process, photolithography or electron beam lithography is used to create a pattern in a photo resist on a wafer surface. A chemical precursor polydimethylsiloxane
(PMDS) is spin coated onto the surface of the pattern. This is then cured into a robust solid. The PMDS replica can then be used to reproduce the patterns. This process can replicate structures less than 10nm which is well suited for the fabrication of subwavelength optical devices, waveguides, optical polarizers etc. In assembling of one dimensional structures or nanowires, Huang and co-workers [116] were the first to demonstrate the use of this technique. In their work, they showed that nanowires can be assembled into parallel arrays with control over the average separation and the complex crossed network of nanowires arrays can be prepared using layer by layer assembly with different flow direction of subsequent steps [116]. Electrical transport studies of the network reveals that each crossed junction forms an individually addressable devices function. Their work has shown that nanofluidic assembly of nanowires offers the potential of assembling single devices into an integrated circuit on a chip and is advantageous over the other assembly processes. This method provides an assembly technique for any kind of one dimensional structure and also allows the fabrication of complex geometrical network by careful control of the angles between the directions of the sequential steps. This has opened up the possibility of fabricating nanodevices such as nanosensors, nanolaser and even nanoscale logic circuits as discussed in section 1.3.2.

1.4.2 Magnetic/Electric-field assisted assembly

Duan and coworkers [22,115] were the first to demonstrate the use of an electric field to assemble a network of doped InP and Si nanowires to measure the I–V characteristics. Crossed-wire junctions were obtained by using diametrically opposed electrodes to align the second layer of nanowires perpendicular to the first layer. This technique was used to assemble
gold nanowires as well [117]. An external magnetic field was used to assembly nickel nanowires [118], but this process is complicated by the use of extensive lithography to fabricate the electrodes needed to generate the microscopic electric fields.

1.4.3 Scanning Probe Manipulation

Scanning Probe Microscope (SPM) has been demonstrated to even make possible manipulation of atoms. Researchers at IBM using a special SPM scanning tunneling microscope have shown that nearly perfect atomic patterns, like the quantum coral, can be created. So it should be anticipated that an AFM can also be used to manipulate the larger nanowires, as long as the force between the wire and the substrate can be overcome. Of course, using an AFM for circuit construction is too labor intensive for large scale devices. It use is therefore restricted to small scale circuits, probably for fundamental, rather than practical importance. Most of the early work on the electrical transport studies in low dimensional systems such as carbon nanotubes relied on putting contact pads on a substrate and randomly dispersing the nanotubes with the hope that a nanotube by chance will align properly across the contact pads [119-122]. Contacting by chance, give way to manipulation and assembly by AFM. In contact mode, the AFM tip was used to push and manipulate the nanotube into desired configuration. It has been used to assemble nanotube cross junction for electrical transport measurement [123] and even in manipulating single-walled carbon nanotubes (SWNTs) to form Greek letters [124]. The biggest draw back is the time involved in the manipulation process. It takes a lot of time in moving the nanotubes around, thus limiting it use in assembly of nanostructures.
1.5 Thesis Structure

In Chapter 1, I have given an introduction to the field of nanowire research trying to motivate my thesis research that will follow. Chapter 2 will focus on the details of the nanowires synthesis methods that I have developed here at PennState. I will discuss the specific growth conditions and the parameters that affect the growth process, crystallinity and diameters of several nanowire systems. The unifying principle is the Vapor-Liquid-Solid (VLS) growth mechanism. Chapter 3 will address the general characterization of the atomic structure and morphology of the nanowires. It will also describe experimental details of the instruments used to characterize the wires structurally and optically. In Chapter 4, I will review the theory of Raman scattering and its application to phonon confinement. Fano resonance scattering is also important to this thesis, and will be discussed. In fact, I will finally propose a unified Fano-phonon confinement model to explain laser power dependent scattering in confined nanowires. In the subsequent chapters; 5,6,7 and 8, the discussion in chapter 4 will be applied to Si and Ge nanowires that I have grown and studied. Finally in chapter 9, I will discuss a new form of NW, “twinning superlattice” nanowires of GaAs.
REFERENCES


Chapter 2

Synthesis of Semiconductor Nanowires

2.1 Introduction

In this Chapter, I will discuss the method of Pulsed Laser Vaporization (PLV) to synthesize Ge and Si nanowires. I will examine the experimental parameters that determine the constituent ingredient for target material selection, the growth conditions and parameters that affect the nanowire growth, as well as the growth mechanisms as applied to the Si and Ge nanowires.

The advances in whisker technology in the 1970s led to the growth of microstructures long, high aspect ratio of the order < 1µ in diameter. The discovery of carbon nanotube by Iijima in 1991[1], the development of pulsed laser vaporization by Smalley [2], and subsequent theoretical breakthrough on the electronic states by Mintmire, Dresselhaus and others [3-6] initiated an avalanche of interest in the intellectually challenging area of one-dimensional nanostructures. Today, carbon nanotubes remains the best example of perfect (or near perfect) one-dimensional periodic system. In the past decade, however, several other novel one-dimensional nanofilaments such as nanorods, nanowires, nanocables and nanobelts have been synthesized and studied. However, much remains to be learned about the intrinsic and extrinsic properties of these filamentary systems. Successful measurement of some of the physical properties of carbon nanotubes [7-15], and other one dimensional structures [16-19] and the
development of self-assembly techniques have facilitated the fabrication of nanodevices. Very recently considerable attention has been devoted to filamentary systems, where the confining dimension(s) is (are) on the order of 10nm or less. Controlling the intrinsic and the extrinsic properties requires a fundamental understanding of the growth mechanism and how impurities and defects enter the structure. For compound nanowires, e.g. GaAs, the Ga:As stoichiometry must be controlled to high precision as atomic vacancies will also act as impurity centers. This is discussed in Chapter 9. A one-dimensional system is the smallest dimension structures which can be conveniently used for electronic transport and electrically driven devices. They are expected to be critical to the function and integration of nanoscale devices [20]. In principle \( E_g \sim 1/d^\gamma \), where \( d \) is the wire diameter and \( 1.4 \leq \gamma \leq 2 \). For the case of of SWNTs, preliminary research has shown that metallic SWNTs can be separated from semiconducting SWNTs. However, we cannot (as yet) set out to grow a semiconducting carbon nanotube at a specific site.

In the past decade, different growth mechanisms have being developed to synthesize a variety of nanostructures. These include Vapor-Liquid-Solid (VLS), Solution-Liquid-Solid (SLS), Oxide-assisted, solvothermal, thermalization, templates and membranes approaches. This section will discuss most of these synthesis techniques and their importance in the nanostructure growth processes.

### 2.1.1 Vapor-Solid-Liquid (VLS) Growth Mechanism

VLS growth mechanism is a vapor-phase based synthesis method. Among all the vapor-phase methods, VLS is one of the most successful and widely used techniques in synthesizing
single crystalline and polycrystalline semiconductor nanostructures in large quantities. In the PLV system, the VLS growth mechanism is a four step process: 1) a semiconductor/metal target is ablated by the laser to generate the plume which contains metal rich molecular-clusters of semiconductor/metal and semiconductor vapor. 2) the cluster size develops, absorbing semiconductor vapor and becomes supersaturated. 3) the excess semiconductor then precipitates at the metal particle surface to form the wires. This is schematically shown in Figure 2–1. Details of the growth and the required conditions are discussed in section 2.2.6.2.

The VLS growth mechanism was first proposed by Wagner and co-workers [21] for semiconductor whiskers growth, and was further described in detail by Wagner and co-workers [21-23], Givargizov [24-26] and Chernov [26]. The whiskers grown by this mechanism in a Chemical Vapor Deposition (CVD) [27] apparatus were tens of microns in diameter, scaling with the diameter of metal particles used to nucleate the whiskers growth. To produce structures of few nanometers in diameter (< 10nm) and tens of µm long, precursors leading to particle size of 4-20nm have been developed. The semiconductor feed stock can come from CVD or laser vaporization. The VLS growth mechanism has successfully been used to fabricate elemental: e.g., Si [28-33] and Ge [29,32,34], binary: e.g., GaAs [29,32,35,36], GaN [29,32,37] and ternary compounds: e.g., AlGaAs [29] nanowires. In this work, the VLS mechanism is used in the growth of the Ge and Si nanowires in a PLV synthesis apparatus.
2.1.2 Solution-Liquid-Solid- (SLS) Growth Mechanism

The SLS growth mechanism is similar to the VLS. However, in SLS all the precursors are in a solution where the nanowire growth takes place. This approach was first explored by Buhro and co-worker [38-40] and used for synthesizing highly crystalline nanowires of III-V semiconductors at relatively low temperatures. A schematic of this growth mechanism is shown in Figure 2–2. In a typical SLS growth process, a low melting point metal (such as In, Bi Sn) is used as catalyst and the semiconductor material is generated by decomposition of its organometallic precursors. This process mostly generates single crystalline nanowires of diameter ranging from 10nm to 150nm, and tens of microns long. In principle, the operation
temperature of the synthesis process can be reduced to temperatures well below the boiling points of the commonly used aromatic solvents. For example, methanolysis of \(\{\text{tert-Bu}_2\text{In}[\mu-\text{P(SiMe}_3)_2]\}\) in an aromatic solvent yield polycrystalline InP nanowires ranging from 10nm-100nm in diameter and tens of microns long at temperatures in the range of 111−203 °C [40,41]. This suggests that the SLS growth mechanism can be modified to operate at temperatures well below that of VLS. The SLS route have been used to synthesize both binary and ternary semiconductor nanowires as well [38-40]. One challenging problem in the SLS growth mechanism is synthesizing nanowires of diameters below 10nm. In 2003, Korgel and coworkers[42, 43] demonstrated this by using a supercritical fluid (organosilane precursor in the presence of sterically stabilized gold nanocrystals) as a solvent in the SLS process to fabricate defect free Si nanowires with nearly uniform diameter of 4nm-5nm and tens of microns in length. In this process, a precursor solution composed of alkanethiol-passivated Au nanocrystals [44] and a liquid Si precursor (diaphenylsilane) is mixed with a preheated and pre-pressurized supercritical hexane (typically at ~ 500°C and 20MPa) in a Titanium reactor.

\[R_3M + EH_3 \rightarrow \text{flux droplet} \rightarrow \text{M.E} \rightarrow 3 \text{RH} \rightarrow \text{Solution} \rightarrow \text{Liquid} \rightarrow \text{Solid} \]

*Figure 2–2: Schematic of SLS growth mechanism. The growth process is similar to the VLS, however, the process takes place in solution.*
2.1.3 Oxide-Assisted Growth Mechanism

One of the advantages of the oxide-assisted growth mechanism is that it does not require metal particle needed in the VLS approach. This eliminates any contamination by the metal may occur in VLS growth. Lee and co-workers [45] were the first to report the synthesis of nanowires by this mechanism. They employed a mixture of a semiconductor and its oxide to prepare the target used for the PLV system. For example, in synthesizing Si nanowires, a Si/SiO$_2$ mixture was used [45]. They proposed that the intermediate state Si,O (x > 1) in the vapor-phase seems to be the key ingredient in the nanowire formation. They proposed a three step reaction process as follows:

$$x\text{Si} + \text{SiO}_2 \rightarrow 2\text{Si}_x\text{O} \quad (x > 1)$$

$$\text{Si}_x\text{O} \rightarrow \text{Si}_{x-1} + \text{SiO}$$

$$2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$$

Lee and co-workers suggested a number of factors that might determine the growth kinetics. For example, the growth tip of the nanowire, which is highly rich in Si$_x$O, that indicates Si$_x$O has an effect similar to the metal in the VLS mechanism. They have also used the oxide assisted growth to fabricate GaAs nanowires of diameter ranging from 10nm to 120nm using GaAs/Ga$_2$O$_3$[36] target in a PLV system.

In other related studies, Lieber and co-workers synthesized MgO nanowires by a carbon thermal reduction process where Mg vapor was generated by reducing MgO with carbon. The Mg vapor was further oxidized to form the MgO nanowires [46,47]. Other binary oxides such as Al$_2$O$_3$, ZnO and SnO$_2$ have been synthesized by this method [48,49]. Yang and co-worker
fabricated CuS nanowires by oxidizing Cu into Cu$_2$O using O$_2$ gas and then treating the intermediate oxide with H$_2$S under ambient conditions to form the CuS nanowires [50].

### 2.1.4 Solvothermal Growth Mechanism

In a solvothermal growth mechanism, the synthesis process utilizes a solvent under pressure and temperature above its critical point to increase the solubility of the solid as well as to increase the reaction kinetic rate between the solids. Heath and co-worker [51] were the first to use this technique to synthesized semiconductor nanowires. They fabricated Ge nanowires by reducing GeCl$_4$ or phynol-GeCl$_3$ with Na in an alkane solvent at a temperature of 275$^\circ$C and pressure of 100atm [51]. This method have also been employed by Xie, Li, Qian and co-workers to fabricate a variety of nanowires [52], nanotubes [53-55] and whiskers [56-58]. One disadvantage of this process found so far is the low yield, poor quality and non-uniformity in diameter of the nanostructure product.

### 2.1.5 Direct Vapor Phase Mechanism: Thermalization

Thermalization, a direct evaporation process have been employed by many researches to synthesize one dimensional nanostructures. Zhu and co-workers used this method at elevated temperatures to synthesize Si$_3$N$_4$, SiC, Ga$_2$O$_3$ and ZnO nanowires by thermalizing the commercially available powder [59]. In addition, this method has been used to fabricate nanobelts or nanoribbons [60] of a uniform rectangular cross section. Most of these nanobelts were single crystal, highly pure in elemental and phase compositions and were said free from
defects and dislocations. Their typical width ranges from 30nm to 300nm and a ~ 5-10 width to thickness ratio was reported. By mixing metal and semiconductor powder our group has used thermally driven vaporization to produce GaAs nanowires that exhibit a twinning superlattice. Figure 2–3. The twinning density was found to increase with decreasing nanowire diameter. An important aspect of the twinning superlattice is that the predicted bandgap should depend on the density of the twinning, shifting to lower energy with increasing twinning. Thus twinned structures of many wide band gap semiconductors can be fabricated to exhibit visible and IR characteristics; the importance of such structures in photo-detection and optoelectronics cannot be over emphasized.

Figure 2–3: Twinning bands of GaAs nanowires showing the lattice fringes of the twinning bands. The twinning density depends on the wire diameter.
2.1.6 Template-Directed Growth Mechanism

The template-directed growth mechanism is one of the preferred techniques for synthesis of nanostructures. This technique offers a way of producing nanostructures with a narrow diameter distribution. The template serves as a scaffold and the nanostructures mimic to some degree the features of the template surface. There are various templating techniques. These include: step edges, channels in porous membranes, self-assembly, etc. The drawbacks of this approach seem to be that the nanostructures that are produced are often polycrystalline.

2.1.6.1 Using Surface Features on Template

Surface features on templates provide a powerful route for the synthesis of various metallic and semiconductor nanowires [61]. By using a shadow sputtering technique of metals source against V-groves array (Figure 2–4A) on the surface of Si (100) wafer, Jorritsma and co-workers [62-64] fabricated metal nanowires (Au, Ag, Cu etc.) as small as 15nm. Another techniques that has been employed is direct vapor-phase deposition by Molecular Beam Epitaxy (MBE) into the groves, or by solution-phase electroplating (Figure 2–4B) [65, 66]. Using this approach Muller and co-worker [67] demonstrated the fabrication of parallel arrays of Ge nanowires and Sugawara and co-worker [68] have synthesized 3 dimensional array of Fe nanowires on the V-grooves of NaCl (110) crystal. Figure 2–4C is cleaved-edges overgrowth that have been used to fabricate metallic and semiconductor nanowires by MBE or electroplating [69]. Using electrodoposition on a step-edge template (Figure 2–4D), Penner and co-workers [70,71] have grown highly oriented pyrolytic graphite (HOPG) as well nanowires of noble
metals (Au, Ag, Cu and Pd), and metal oxides (MnO, CuO and FeO). These oxides could also be reduced in hydrogen to produce their corresponding metallic nanowires [70,71]

![Figure 2–4: Schematics of different surface features that can be used to fabricate both metallic and semiconductor nanowires: A) shadow spattering, B) reconstruction at the bottom of grooves, C) cleaved-edge overgrowth, and D) step edge](image)

2.1.6.2 Using Channels in Porous Membranes

There are two types of commercially available mesoporous membrane, i.e., polymer films and anodic alumina. Martin and co-workers [72-74] were the first to exploit such mesoporous membranes in the synthesis of nanowires. It seems that the only requirement in the synthesis of nanowires by this technique is that the feedstock should be able to diffuse or electrochemically be drawn into the pores or channels in the membranes. Different methods: vapor-phase sputtering, liquid-phase injection, electrochemical deposition, solution-phase
injection and electrophoresis have been employed to fabricate nanowires [74-78]. Figure 2–5 is a schematic showing different route for synthesizing either completely filled or hollow nanowires. Mallouk, and co-workers [79] have demonstrated the use of this method to fabricate nanowires containing well defined different bands of metals. In growing semiconductors nanowires, a metal seed is used and the growth process is governed by VLS.

![Figure 2–5: Schematic of nanoporous membrane synthesis of nanostructures showing two possible routes for synthesis of nanowires of different morphology: filled and hollow.](image)

2.1.6.3 Using Self Assembly of Molecular Structures

Another class of materials that can be used to fabricate nanowires are self-assembly structures such as surfactant molecules which organize themselves spontaneously into rod-shaped or bilayer spherical micelles or inverse micelles when their concentration reach a critical value [80]. Such structures can be used as templates in appropriate chemical or electrochemical reactions. Schematically shown in Figure 2–6 are the routes of using rod shaped micelles and inverse micelles to fabricate filled and hollow nanowires respectively. This method have been
used to fabricate monodispersed BaCrO$_4$, BaSO$_4$ and BaWO$_4$ nanorods as well as Au and Ag nanowires [81-85].

Figure 2–6: Schematic of two routes of self-assembly molecules like surfactant molecules in a form of micelles and inverse micelles to fabricate filled and hollow nanowires.

2.2 Synthesis by Pulsed Laser Vaporization (PLV)

In recent years, PLV has become one of the most versatile synthesis techniques for fabricating low dimensional materials such as semiconductor nanowires, carbon nanotubes, quantum dots and nanoclusters. The diameter of these nanostructures ranges from few nanometers to tens of nanometers. Wires can be produced that are tens of microns long. PLV offers the flexibility in manipulating the synthesis parameters and conditions to control diameter, length and doping levels. Smalley and coworkers in 1996 [86] used this technique to synthesized
Single-Walled and Multi-Walled Carbon nanotubes. Since then, this method has been used to synthesized various types of semiconductor nanowires and nanoislands (nanoparticles) from single element such as Si [87-89] and Ge [90] to ternary compounds like AlGaAs [91]. It can be asserted that, PLV can be used to synthesize nanowires of most of the semiconductor materials.

### 2.2.1 PLV Apparatus used to prepare Si and Ge nanowires

Our Pulsed Laser Vaporization (PLV) apparatus is schematically shown in *Figure 2–7*, and the actual set up is shown in *Figure 2–8*. The system contains three primary components: 1) the pulsed Nd: YAG laser used to vaporize the target material, 2) the optical delay network used to separate the IR (1064 nm), visible (532 nm) and the UV (266nm) harmonics pulses from the laser and 3) the split-tube furnace used to provide thermal assistance for the growth process.

*Figure 2–7*: Schematic of our Pulsed Laser Vaporization apparatus. The IR radiation is delayed relative to the visible and UV radiation using dichroic beam splitters (see *Figure 2–14*). A computer controlled lens is used to scan the beam over the target.
Figure 2–8: Photograph of our PLV system showing the laser, the split tube furnace growth chamber and the enclosure of the delay optics network.

2.2.2 Target preparation

VLS growth requires a metal particle which can dissolve the semiconductor vapor. The semiconductor wire grows as a precipitate attached to the metal particle. Therefore, the particle has to be either pre-installed in the tube furnace (on a substrate) and the target/laser provides the semiconductor vapor, or we have to add the metal to the target and hope that the vaporization of the target produces small metal particles. Fortunately, the later approach is not as difficult as it seems. A particular metal that dissolves the semiconductor is selected by studying the phase diagram of the constituent components (section 2.2.6). In the synthesis of Si and Ge nanowires, Gold (Au) or Iron (Fe) was used as the metal solvent and added to the target which is prepared
by mixing their respective powders (semiconductor; size: 5µ−20µ, purity: 99.999%, metal; size: 0.8µ−1.5µ, purity 99.999% from Alfa Aesar) thoroughly using a Ball Mill (see Figure 2–9) for twenty four hours. The powder is then packed in a pellet press (Figure 2–10) and uni-axial pressure at five metric tons for five hours (Figure 2–11) was applied. The target as a pellet was removed from the press and mounted in a carbon target holder (see Figure 2–12) and then place in the 1.00" quartz tube (Figure 2–17).

Figure 2–9: Ball mill used in semiconductor/metal mixing. The mixing chamber is a simple glass jar surrounded by two O-rings to facilitate rotation.
Figure 2–10: The parts of the pellet die (made from hard steel) used to form the mixed-powder targets using a hydraulic press (Figure 2–11).

Figure 2–11: left) Pellet press (die) schematic and right) hydraulic from used to press the target at five metric tons.
Figure 2-12: Images of a) freshly prepared target (0.50" by 0.25" thick), b) target holder machined from carbon, c) a mounted Si:Fe protruding from the holder, d) ablated target, note the "machined" path on the surface and e) schematic of the computer controlled path of the Nd:YAG beam on the face of the target.
2.2.3 The Laser System

In Figure 2–7, we showed a schematic diagram of the Pulsed Nd: YAG laser (model SL803; Spectron Laser Systems Inc.). The laser has a fixed repetition rate of 10Hz and beam diameter of 8mm (Figure 2–13). The laser has a dual oscillator design: Gaussian and telescopic resonator options with the ability to interchange between the two.

Figure 2–13: Spectron Laser Systems Pulsed Nd: YAG laser, model SL803 used in the synthesis of Ge and Si nanowires. Specifications are given in Table 2.1. The output beam(top) indicates the possible wavelength combinations, depending on how the laser is configured.
This configuration provides a nearly uniform $\text{TM}_{\infty}$ beam with high energy and low divergence. The telescopic resonator provides a larger fraction of the beam energy in the fundamental $\text{TM}_{\infty}$ mode compared to a conventional stable resonator of similar length. This is achieved by employing a telescopic optics that reduces the diameter of the intra-cavity beam. The optics limits divergence by decreasing the transverse mode $\text{TM}_{01}$ content in the beam. For such a mode purity from the laser (i.e. ~ 100% $\text{TM}_{\infty}$), we can expect nearly a diffraction limited focal spot size ($d \sim \lambda$) on the target using an external lens (Figure 2–7). If a larger spot size on the target is desired we defocus the beam with the external lens. Typical spot diameters $d$ in the range between $2\text{mm} < d < 1\mu$. Such spot size flexibility is critical in PLV nanowire synthesis technique as we shall see. Our pulsed Nd:YAG laser has three output wavelengths: the fundamental (first harmonic at 1064nm), second harmonic (at 532nm) and the third harmonic (at 355nm). The output at 1064nm is 850mJ per pulse with pulse duration of $13 \pm 2\text{ns}$ (FWHM). The second harmonic at 532nm has 320mJ per pulse and pulse duration at FWHM of $12\pm2\text{ns}$ (FWHM). The third harmonic at 355nm has 140mJ per pulse and pulse duration of $11\pm2\text{ns}$ (FWHM). Each laser frequency can be used independently, depending on a particular experimental requirement or they can be combined into one beam overlap in space and time. Details of the laser specifications are given in Table 2–1.
Table 2–1: Specifications of the Model SL803 Spectron Laser Systems Nd: YAG Laser

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Pulse Energy (mJ)</th>
<th>Pulse Duration (FWHM)(ns)±2</th>
<th>Energy Stability pulse-pulse(±%)</th>
<th>Power Drift (over 8 hours) (±%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>850</td>
<td>13</td>
<td>&lt; 2</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>532</td>
<td>320</td>
<td>12</td>
<td>&lt; 4</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>355</td>
<td>140</td>
<td>11</td>
<td>&lt; 6</td>
<td>&lt; 6</td>
</tr>
</tbody>
</table>

2.2.4 External Optical Delay

In the PLV synthesis of our nanowires, only the fundamental and the second harmonic have been used. In the PLV synthesis of carbon nanotubes, Smalley and co-workers suggested that it was desirable to have the second harmonic pulse (532nm) hit the target first, followed by the fundamental (1064nm). The thinking was that the higher photon energy at 532nm would ablate the target best and the following IR beam would heat the plume created by the vis pulse. The benefit of this time separation really makes is debatable. However, we have followed this approach. The time delay in the IR beam is made using the optics shown schematically in Figure 2–14. The output beam from the laser contains both the fundamental and the second harmonic (the UV amplifier was disabled). The IR and the visible pulses were separated into component by
a dichroic beam splitter as shown in Figure 2–14. The 1064nm beam is transmitted and the 532nm beam is reflected, as shown. The fundamental beam was optically delayed by forcing it to follow a longer path length before being recombined with the visible beam. By adjusting the angle of incidence of the 1064nm beam on the pair of parallel mirrors (M3 and M4), the delay can be changed to suit a particular experiment. The two laser beams are then recombined with a second dichroic beam splitter and then focused onto the target by a computer-controlled lens as shown in Figure 2–15. The lens is translated in a plane perpendicular to the beam direction maintaining the target to lens distance.

Figure 2–14: schematic of optical delay network showing the harmonics separation optics, the delay optics and the recombination optics.

In the case of Ge and Si nanowires, a 50ns delay time was used. As explained in chapter one, section 1.1, equation 1.1, the diameter of the nanowire is dictated by the diameter of the liquid
metal droplet in the growth chamber. For reasons that are not fully understood, a reasonably narrow diameter distribution of metal “seeds” for the nanowires growth can be obtained simply by adding metal to the semiconductor target. The particle size depends on many experimental parameters. The most important appears to be the pressure of the background gas in the growth zone.

\[\text{Figure 2–15: Actual set up of the optical delay system. The labels correspond to that on the schematic in Figure 2–14.}\]

\[\text{2.2.5 The Nanowire Growth Chamber}\]

The quartz growth chamber used in our PLV nanowire synthesis resides inside a differential three-zone, split-tube furnace (model HZS 12/600; Carbolite Inc.) with a 1200°C maximum temperature. The target is centered inside a 1.00" diameter inner quartz tube which fit inside a 2.00" diameter outer quartz tube, as shown schematically in Figure 2–16. The pressure control and flow rate of a background gas that passes down the inner tube is electronic performed
by an MKS type 640 (pressure controller) and type 624 (mass flow gage). The flow meters are
coupled to four channel readout (MKS, type 247). The inner quartz tube is centered in the outer
quartz tube using carbon rings (Poco Graphite Inc., pg-0.5-12). These carbon supports also serve
to reduce heat loss down the axis of the split tube furnace. Vacuum tight seals to the outer quartz
tube are made via O-rings in machined aluminum flanges shown in Figure 2−17 b, c.

For the case of Si and Ge nanowires, growth was carried out in Ar/H\textsubscript{2} mix, 90:10. The
mixed gas is pre-heated \textit{in situ} by admitting it into the outside tube, and passing it down through
the entire heated length of the furnace and then back through the inner tube flowing by the target
(Figure 2−16). This configuration ensures that the target temperature is not as sensitive to gas
flow rate as it would be if the gas were to enter the inner tube at room temperature. A
temperature fluctuation in the inner tube might adversely change the metal particle seed
formation or the diameter distribution. The growth apparatus is shown in \textit{Figure 2−17}. We
regulate the gas flow and the pressure with an MKS baratron transducer (type 626).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Schematic of the growth chamber, showing the in situ preheating gas configuration, the target position, the inner tube and the outer tube}
\end{figure}
2.2.6 Vapor Liquid Solid (VLS) applied to Si and Ge nanowires

The Vapor-Liquid-Solid (VLS) mechanism for crystal growth was first proposed by Wagner and co-worker [21] to explain the crystal growth of Whiskers in general, and Silicon whiskers in particular. Whiskers are polycrystalline filaments with a faceted cross section. The term originally was used to describe filaments with diameters in the range 10µ-100µ. The lengths usually exceeded many microns and even in millimeters. The VLS process was described
in further detail by Wagner and co-worker [21-23], Givargizov [24-26] and Chernov and Givargizov [26]. In general the VLS mechanism involves a small metal particle that can dissolve the material which one would want to reform as a filament. The temperature of the particle is chosen so that the particle with dissolved ingredient is a liquid (binary alloy). Once the particle is in contact with the vapor, it will eventually form a liquid droplet, then, saturation with semiconductor causes the filament to grow as a surface precipitate. For example, using Gold, as a solvent, Wagner and co-workers [21-23] proposed a two step process for the growth of Si whiskers: the formation of a liquid solution in a vapor-liquid system, and precipitation from the supersaturated liquid solution at the liquid-solid interface. He explained that the Au/Si (Au_{1-x}Si_x) system has a low eutectic temperature at 361°C and thus would form a whisker for temperatures greater than 361°C, if sufficient Si was added to the Au particle. A constant supply of Si from the vapor phase eventually saturates the clusters. At supersaturation, excess Silicon necessarily precipitates to form the Si whiskers that are attached to the particle. The diameter of the whiskers was found to be limited by the radius of the initial particle diameter. Whiskers of Si were produced by this method with diameter in the range of 10µ-100µ.

To make nanoscale materials of diameter ranging from few nanometers to tens of nanometers, a similar but small diameter particle is required. Vaporizing a metal loaded target (e.g., 5% Au or Fe in Si) was found to lead to the production of \( d \geq 10 \)nm diameter Au-Si droplets that by VLS produced \( d \geq 8 \)nm diameter Si nanowires. The main experimental parameters of the PLV process that we feel affect the quantity and crystallinity of the nanowires are the pressure, growth temperature in the tube furnace, inert gas flow rate and the particular metal solvent used. For example, Fe also does a good job in the VLS synthesis of Si nanowires,
although the eutectic temperature for Fe:Si is quite higher (~1105°C) than that of Au: Si (~363°C). Growth temperature, where a liquid alloy particle should produce VLS growth can be deduced from the equilibrium binary phase diagram.

2.2.6.1 Pseudo-Binary Phase Diagram for Ge:Au and Si:Au systems

Phase diagrams provide us with the information to predict if a metal/semiconductor target will induce VLS growth in PLV. As mentioned above, the metal-semiconductor particle should be a liquid under nanowire growth conditions. In many cases, a minimum melting point composition at a temperature compatible with the furnace is a necessary condition for VLS. This particular composition is called the “eutectic”. In Figure 2–18 [92] we show the phase diagram of Ge-Au, the eutectic composition is seen to be ~28 at. % Au in Ge. The phase diagram for Si-Au is similar, and is shown in Figure 2–19 [92]. Both phase diagrams have almost the same eutectic temperature (that is, the temperature at which all the three phase exist in equilibrium) at 361°C and 363°C for Au-Ge and Au-Si systems, respectively. In theory, any temperature above the eutectic point is suitable for Si or Ge nanowire growth. However, lower synthesis temperatures tend to produce more defects in the nanowires. The details of the phase diagram are given in Figure 2-20 to explain the nanowire growth mechanism. In the synthesis of Si and Ge nanowires, the phase diagrams shown in Figures 2–18 and 2–19 indicate that Au is an ideal candidate for Si, Ge nanowire growth for two reasons: one cannot form solid state AuSi, AuGe compounds for T > 500°C. Higher growth temperatures are advisable for kinetic reasons (liquid diffusion and growth). Higher temperatures also reduce the formation of defects such as strains and faults.
Figure 2–18: Phase diagram of Au-Ge system showing the melting point of pure Au (1064° C), the melting point of pure Ge (937° C) and the four distinct regions separated by the freezing point depression curves and the eutectic temperature [92] line.
Figure 2–19: Phase diagram of Au-Si system. Indicated on the diagram is the eutectic temperature (363°C), the melting points of Au (1064°C) and Si (1414°C) and the eutectic composition [92].
2.2.6.2 VLS Growth Mechanism for Si Nanowires

Since both Au-Si and Au-Ge have similar phase diagrams, we discuss the VLS growth for Si nanowires only. Ge nanowires grow analogously. In Figure 2–20, the curves AE and JE are the melting (freezing) point depression of Au due to Si, and Si due to Au, respectively. Point E is the eutectic point (a three phase point where pure solid gold (Au)$_s$, pure solid silicon (Si)$_s$ and gold-silicon liquid (Au-Si)$_l$ are at equilibrium. The line DEF at the eutectic temperature separates the solid phases below the line from liquid phases above the line. Four distinct phase regions (U, X, Y, Z) can be identified in Figure 2–20: region Y is a single-phase region of Au-Si liquid (Au-Si)$_l$; X is a two phase region of solid gold (Au)$_s$ and (Au-Si)$_l$; Z is a two phase-region of solid silicon (Si)$_s$ and (Au-Si)$_l$ and region U is a two-phase mixture of solid gold (Au)$_s$ and solid silicon (Si)$_s$. At any temperature below the eutectic, it can be seen that the semiconductor phase and Au phase must separate. The dashed horizontal line represents the growth temperature established at the center of the furnace near the target. The plume of ejected vapor from the target may be initially hotter than the furnace temperature, but the furnace temperature has a significant impact on the wire growth, and it appears that the droplets approach the temperature of the furnace before the wire growth proceeds. In other words, it is the furnace temperature, and not the initial plume temperature generated by the laser that controls wire growth. At a study state C, absorption of Si from the vapor phase occurs. As this process continues, the composition of the cluster changes till it reaches point I on the Si freezing point depression curve, where further absorption of Si vapor leads to supersaturation that drives Si precipitation in a form of nanowires. Thus a continuous absorption of Si vapor followed by supersaturation and precipitation leads to a continuous growth of the nanowires as illustrated schematically in Figure
2-1. As the wires drift via the inert gas flow to colder regions of the furnace, the droplets freeze and the VLS growth stops.

Figure 2–20: illustrate the details of the eutectic diagram of Au-Si system. The curve AE and JE are the freezing point depression of Au due to Si and Si due to Au respectively. The point E is the eutectic point. The region marked Y is a single phase region of Au-Si liquid, X is a two phase region of solid Au and Au-Si liquid, region Z is a two phase region of solid Si and Au-Si liquid, and region U is a two phase mixture of pure solid Au and pure Solid Si.
2.3 Growth Chamber Pressure and the Nanowire Diameter

The main growth parameters that govern the growth of nanowires are pressure, gas flow rate, temperature and the power density of the laser on the target. For Si and Ge, the temperature and flow rate mostly affect the nanowire crystallinity. Early preliminary studies showed that pressure fluctuations in the growth chamber lead to formation of amorphous nanowires, so we added electronic pressure control. The gas flow rate influences both quality and crystallinity of the nanowires as well. Too high a flow rate appears to terminate the growth pre-maturely. On the other hand, too low a flow rate prevents the plume from reaching the optimal growth region downstream.

The control of the diameter of the nanowires has been proposed [24-26] to be governed by a Gibbs-Thomson relation that describes the relationship between the nanowire diameter, the system vapor pressure and surface energy of the clusters at supersaturation. The relation imposes a critical lower limit on the diameter of the nanowires formed. The decrease in supersaturation expressed as a function of the nanowire diameter\((D)\) is given by equation 2.1 [24-26].

\[
\frac{\Delta \mu_{NW}}{k_B T} = \frac{\Delta \mu_{BK}}{k_B T} + \frac{4 \Omega \alpha_{cr}}{k_B T d} \tag{2.1}
\]

where

\[
\Delta \mu_{NW} = \mu_{NW} - \mu_v
\]

\[
\Delta \mu_{BK} = \mu_{BK} - \mu_v \tag{2.2}
\]

\(\mu_{NW}, \mu_{BK}\) and \(\mu_v\) are the effective chemical potentials of the nanowire, the bulk and the vapor phase respectively. \(T\) is the growth temperature in Kelvin, \(k_B\) is the Boltzmann constant, \(\Omega\) is the
atomic volume of the nanowire element and $\alpha_{vs}$ is the specific surface free energy of the nanowire. Presumably, there is little or no difference in these values for the nanowires from the bulk.

The above equations impose a condition on the critical size of the nanocluster. Below the critical diameter, there will be no formation of the nanowires. Thus, for very small cluster diameters, nanowire growth is not feasible because of a large surface to volume ratio. This leads to a higher effective chemical potential for the nanowire than the effective vapor phase chemical potential. Nanowire growth then only becomes feasible when the nanocluster size increases (via agglomeration for example) and reaches the critical diameter. From equations 2.1 and 2.2, it is apparent that for any experimental conditions, there will be a minimum nanowire diameter but it is nevertheless possible to synthesize a wide range of nanowires with diameters greater than this minimum critical diameter. Thus, the nanowire diameter distribution is often times found to exhibit a log-normal characteristic, as shown in Figure 2–21. Increasing the vapor pressure increases the effective chemical potential of the vapor phase, making $\Delta\mu_{\text{vac}}$ more negative which initiates smaller diameter nanowire growth. Thus increasing pressure should cause a corresponding decrease in the diameter of the nanowires. Although we have not undertaken quantitative studies of equations 2.1 and 2.2 in this work on Si and Ge nanowires, we have observed qualitative agreement with these equations. For example, the wire diameter was observed to decrease with increasing the Ar/H$_2$ pressure in the growth chamber.
**Figure 2–21**: A typical “log-normal” diameter distribution $N(D)$ for our nanowires. The arrow indicates the diameter limit imposed by the experimental conditions. The functional form is given by $N(D) = \left(\frac{1}{\log_{10} \sigma}\right) \sqrt{2\pi} \exp\left(\frac{(\log_{10} d - \log_{10} d_o)^2}{2(\log_{10} \sigma)^2}\right)$. The top arrow indicates the most probable diameter.

### 2.4 Experimental Procedure for Si and Ge Nanowire Growth by PLV

As shown schematically in Figure 2–16 the pressed pellet target is centered in the 1.00" quartz and held there by the carbon pellet holder (Figure 2–12). Details regarding target
preparation appear earlier in this chapter. The system is then sealed and evacuated by rotary (mechanical) pump. The electronics are shown schematically in Figure 2–22. An electronic feedback loop, used to set the values of the gas flow rate and the pressure is contained in a four channel readout (MKS, Model #247). The pressure controller (MKS model #640) is connected downstream while the mass flow controller (MKS model #624) is connected upstream. In addition, an auxiliary pressure sensor (MKS Baratron transducer model #626) coupled to a readout (Teranove model #809) is connected upstream just before the target. This is used to monitor the pressure of the growth chamber and also as a cross check to the pressure set on the pressure controller (MKS model #640) connected downstream (see Figures 2–16 and 2–17). As explained in the previous section, pressure is the main determining factor of the nanowire diameter. For both Si and Ge nanowire synthesis: gas flow rate, 100sccm and pressure, 100 Torr. The system was pumped down to 10-20mTorr pressure range for one hour and was then purged with Ultra High Purity (UHP) Argon or H₂/Ar mix, 10:90 (99.9999% from MG industries general store) for another one hour. The furnace was heated at 10°C per minute ramp rate. For Si nanowire growth, the temperature on the Carbolite Inc. split tube furnace (model HZS 12/600) was set at 1150°C (with 1175°C as the over temperature set point). For Ge nanowire growth, lower temperature ~ 800°C (with 825°C over temperature set point) was needed. See Table 2–2 for growth parameters and conditions. The over temperature set point prevents the furnace from destructive over heating due to thermocouple failure in the main controller. The temperature profile at 1200°C of the growth chamber is shown in Figure 2–23. The set point temperature was ~ 25°C higher than the maximum temperature read by a calibrated Inconel-sheathed N-type thermocouple. This suggests that without using the double quartz tube reactor for preheating gas
the gas, the difference in temperature between the furnace thermocouple and the growth zone can be quite high.

Figure 2–22: Schematic of the electronics (gas and pressure) controlling the growth conditions. The baratron pressure gauge (MKS model#626) and the T/C gauge (not shown) are connected upstream whereas the gas and the pressure controllers are connected downstream.

When the system reaches the temperature set point, the chamber was heated for an extra one hour before the target is ablated with the laser. A 2mm laser beam spot on the target was used. The growth was carried out for two hours, and then the furnace was cooled at a rate of 20 °C per minute to room temperature. At room temperature, the deposit inside the one 1.00" quartz tube was collected separately every inch or so for characterization. The nanowires started to deposit 6” behind the target (downstream).
Table 2–2: Si and Ge nanowire growth parameters

<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic agent</td>
<td>Au</td>
<td>Au</td>
</tr>
<tr>
<td>Target atomic composition</td>
<td>Ge: Au→90:10</td>
<td>Si: Au→90:10</td>
</tr>
<tr>
<td>Synthesis pressure</td>
<td>100 Torr</td>
<td>100 Torr</td>
</tr>
<tr>
<td>Gas</td>
<td>UHP Argon</td>
<td>UHP Argon</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>100 sccm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>Laser lines</td>
<td>532 nm/1064 nm</td>
<td>532 nm/1064 nm</td>
</tr>
<tr>
<td>Laser energy</td>
<td>320 mJ/850 mJ</td>
<td>320 mJ/850 mJ</td>
</tr>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>
Figure 2–23: Temperature profile of the growth chamber. The profile above is drawn to scale relative to the schematic apparatus (below).
REFERENCES


3.1 Introduction

The development and synthesis of complex nanomaterials requires characterization tools and techniques that will reveal the intricate nature in their structural features and physical properties. To understand the structure and physical properties many characterization tools and techniques of different sophistication have being developed. This chapter focuses on those characterization techniques and we have used for Ge and Si nanowires.

Defects, strain, doping, disorder, etc. can alter the nature of the observed physical properties of solids in general, and nanowires in particular. Therefore, we must carefully characterize the morphology and structure of our nanowires. Indeed even the diameter distribution is crucial information for this thesis. In this work, SEM, TEM, and AFM were used to study morphology, crystal structure, growth direction and diameter distribution of our NWs. Raman spectroscopy was used to probe the optical phonons. In TEM, information can be deduced either from electron diffraction patterns or from direct high-resolution lattice images. AFM and TEM were both used to determine the diameter and length distributions of the nanowires. SEM was used as a tool to observe the typical wire length and the particle contamination in the sample (i.e., small nanoparticles are sometimes grown).
3.2 Sample Preparation for Characterization

Ge or Si nanowires collected from the inner quartz tube were suspended in solution: ~0.5mg was added to ~2ml of ethanol. The solution + nanowires were sonicated at 50 °C in a VWR ultrasonic bath (model P250HT) for 30min. The ultrasound produced a meta stable suspension that was further sonicated using an ultrasonic horn with tip 3mm diameter, Misonix Inc. (model XL 2010). The horn was operated at 100W for 10min. For TEM analysis a drop of the suspension was put on a TEM grid (lacey carbon, EMS) and was dried in air. The grid was ready for analysis after an hour. For SEM analysis, a drop of the suspension was put on a Si substrate and was dried in air for 30min, and then coated with few Angstroms of gold. For AFM imaging, however, the substrate, Si wafer was first spin coated with 3-aminopropyltriethoxysilane (APS) to produce a more highly dispersed set of nanowires on the substrate. The suspension was further diluted (1drop to 2ml of ethanol), and a drop was placed on the coated substrate to dry in air before performing the AFM imaging. For Raman scattering samples were prepared on Indium foil. A piece of Indium foil ~5mm × 5mm was firmly attached to a glass slide with double scotch tape. A drop of the suspension was put on the Indium foil and was dried in air.

A centrifugation process was used to selectively separate the wires according to size. Basically, large diameter nanowires are centrifugally driven to the bottom of the tube, whereas the smaller diameter wires were found suspended in the supernatant.
3.3 Transmission Electron Microscope (TEM)

Our understanding of materials down to atomic levels in terms of processing, structure, and properties has being revolutionized by Electron microscopy. JEOL (JEM 2010) Transmission Electron Microscope operated at 100 keV was used to study our Ge and Si nanowires. Shown in Figure 3–1a and Figure 3–1b are the low-resolution TEM images of Si and Ge nanowires respectively. The corresponding diameter distributions from these and other TEM images from the same batch of sample are shown as histograms plot in Figure 3–1c and Figure 3–1d respectively. The diameters of the nanowires were generated using image analysis software (NIH image software; http://rsb.info.nih.gov/nih-images). Also shown in Figures 3–1c and d are fits to the diameter distribution using a log-normal function, \( F(d) \), given by the expression in equation[1]

\[
F(d) = \frac{N}{\sqrt{2\pi \log_{10} \sigma}} \exp \left( -\frac{1}{2} \frac{(\log_{10} d - \log_{10} d_o)^2}{(\log_{10} \sigma)^2} \right) \quad (3.1)
\]

with

\[
\log_{10} d_o = \frac{\sum (n) \log_{10} d}{N} \quad (3.2)
\]

and

\[
\log_{10} \sigma = \left\{ \frac{\sum n(\log_{10} d - \log_{10} d_o)^2}{N} \right\} \quad (3.3)
\]

where \( N \) is the total number of wires, \( n \) is the number of wires with diameter \( d \), \( d_o \) is the most probable diameter and \( \sigma \) measures the width of the distribution. The most probable diameter and
σ determined from the fits in the figure are: $d_o = 7.5\,\text{nm}$ and $\sigma = 1.5$ for Ge and $d_o = 6.5\,\text{nm}$ and $\sigma = 1.2$ for Si.

High-resolution transmission electron microscope (HRTEM) image of the samples provide important information relating to crystallinity, interplanar distance, growth direction and thickness of the oxide layer covering these nanowires. It should be recalled that Si and Ge grow oxides of ~ 5 nm thickness at room temperature in air. Shown in Figure 3–2a is an HRTEM image of SiNW with 12nm crystalline core diameter and ~1.0nm oxide coating. A (111) family of planes is seen to be oriented at $20^\circ$ with respect to the growth axis. The interplanar angle between equivalent $\{111\}$ planes is $70^\circ$, suggesting a $<111>$ growth axis for this nanowire. In the case of Ge (Figure 3–2b), the crystalline core is 12nm in diameter with ~2nm oxide layer. For Ge the $\{111\}$ planes in Figure 3–2 are oriented at $45^\circ$ to the growth axis suggesting that the $(110)$ direction is perpendicular to the growth axis. A $(001)$ growth direction is consistent with the observation.
Figure 3–1: TEM images of a) Si and b) Ge nanowires. In both cases the wire diameter ranges from 5nm to 19nm as determined by NIH image software. The diameter distribution are shown in c) and d). The inset shows the growth seed on a Si nanowire, characteristic of VLS growth. The solid curves in c) and d) are log-normal fits: c) $d_o = 8$nm and $\sigma = 1.2$, d) $d_o = 8$nm and $\sigma = 1.5$.
Figure 3–2: a) HRTEM image of Si nanowires showing the \{111\} planes. These planes are oriented at a 20° to the growth direction and the interplanar angle between the \{111\} planes is 70° suggesting <111> growth axis. b) HRTEM of Ge nanowires. The \{110\} lattice planes and the (110) direction are respectively parallel and perpendicular to the growth axis with the \{111\} planes at 45° to the \{110\} planes. A (001) growth direction is consistent with this information.

3.3.1 Electron Diffraction

The arrangement of the diffraction spots in the diffraction pattern depends upon the orientation of the nanowire in the focal plane of the TEM and on the growth direction (e.g., 100 or 111) The \(d\) spacing (interplanar spacing) between planes are determined, since the diffraction spots are associated with the coherent reflection of electrons from the planes. The \(d\) spacing is determined from the expression,

\[
Rd = \lambda L, \quad (3.4)
\]

where \(L\) is the distance between specimen and the photographic imaging plate of the TEM, \(R\) is the separation between a spot and the (0,0,0) central bright spot, \(d\) is the \(d\)-spacing of the parallel
planes and $\lambda$ is the de Broglie wavelength of the electron as determined by the acceleration potential of the TEM.

Both Ge and Si exhibit the diamond structure with a two-atom basis in an fcc lattice. The electron diffraction pattern of Si and Ge are shown in Figure 3–3a and b, respectively. The six fold symmetry of the diffraction pattern for Si (Figure 3–3a) is of the $\{111\}$ planes. However, the symmetry of the diffraction pattern in Figure 3–3b (Ge) indicates reflections are from the $\{110\}$ planes.

Figure 3–3: Selected area diffraction (SAD) a) Si nanowire showing a diffraction pattern from $\{111\}$ planes with [111] zone axis. b) Ge nanowire arising from $\{110\}$ planes which suggest a [001] zone axis.

3.4 Scanning Electron Microscope (SEM)

Scanning Electron Microscope is used to provide a direct image of the topographical nature of the surface from emitted secondary electrons. It employs focusing of a probe beam of high energy electrons, typically 5-50 keV to obtain spatial localization. The primary electron beam is scanned across the sample surface (in this case, nanowires on substrate) and the intensity of the electrons emitted from the sample surface of wide to generate the contrast in the image.
These electrons include backscattered primary electrons and Auger electrons that are due to ionization, and secondary electrons formed from multiple inelastic scattering processes.

Figure 3–4: SEM images of: a) Si nanowires and b) Ge nanowires

Usually the topographical information is obtained from a plot of a secondary electron current reaching a detector versus the position of the scanning probe on the surface. Resolution of the order of 5nm is achievable in modern SEMs. In this work, a Hitachi SEM was used. Shown in Figure 3–4 a and b are the SEM images of Si and Ge nanowires respectively. It is clear from these images that the sample contains primarily nanowires and only few % nanoparticles.

3.5 Atomic Force Microscopy (AFM)

Atomic Force microscopy (AFM) can measure surface roughness almost at atomic scale resolution. The basic structure of the AFM is a flexible cantilever with a sharp tip. It can operate in either the contact or the non-contact modes. In the contact mode, the tip of the AFM can also be used to manipulate (translate, bend and rotate) nanowires or nanotubes [2,3]. In the non-
contact mode, the tip is maintained at a few Å from the surface. The Van der Waals force between the sample surface and the tip of the cantilever cause a very small deflection of the cantilever which is measured optically. A piezoelectric transducer is used to scan the tip over the surface of the sample. Feedback is used to maintain the distance between the tip and the surface. By monitoring the voltages to the three scanners (x,y,z), an image of the surface is directly obtained with depth resolution of 0.01nm and lateral resolution of 0.1nm. In this work, a Multimode Scanning Probe Microscope (Nanoscope III) Veeco Digital Instruments was used to probe the structural features of the nanowires. Figure 3–5 is a schematic representation of an AFM instrument. In Figure 3–6a and b, we shows an AFM image of SiNW and the corresponding diameter distribution respectively. The diameter distribution correlates very well with the data from TEM, Figure 3–1.

Figure 3–5: Schematic representation of an AFM showing most of the important components: the laser, the photo diode, the cantilever, the tip, the oscillator and scanning piezoelectric tube.
Figure 3–6: a) AFM image of SiNWs in a non-contact z-scan mode. b) diameter distribution of the SiNWs from AFM z-scan lateral measurement. The solid curve is a log-normal distribution of the data.

3.6 Experimental Issues in Raman Spectroscopy

The advent of the laser and the development of double and triple monochrometers have made inelastic Raman scattering spectroscopy one of the most powerful and versatile non-destructive optical techniques to probe low frequency elementary excitations in solids. The Raman scattering is a two-photon inelastic scattering process. The measured frequencies are $\omega_i$ and $\omega_s$, where $\omega_i$ and $\omega_s$ are frequencies of the incident and the scattered light, respectively. The Raman frequency shift is $\Delta \omega = \omega_i \pm \omega_s$. The case of $\omega_s > \omega_i$ is called the AntiStokes process, whereas $\omega_s < \omega_i$ is known as Stokes process. For a first order Raman scattering process in a
crystalline system, conservation of momentum requires that only zone center phonons are observed [4-6]. This is discussed in detail in Chapter 4.

### 3.6.1 Resolution and Wavelength Accuracy

Raman spectra for this thesis were collected in a backscattering geometry using a microRaman spectrometer (JY–SA HORIBA, model T64000) with a 640mm focal length subtractive-double pre-monochrometer followed by a 640mm spectrograph with a cooled Charged-Coupled Device (CCD) detector. The excitation and the collection optics in the microRaman configuration are shown schematically in Figure 3–7 and a schematic of the spectrometer optics is shown in Figure 3–8. The excitation radiation from the source (Ar or Ar-Kr laser, not shown) is passed through a plasma filter to remove the associated plasma lines. This incident laser beam then goes through an iris and a spatial filter that also defines a “crisp” circular spot that is imaged onto the sample via the objective. A beam splitter (BS) is required to excite the Raman scattering and collect the backscattering light. The part transmitted through the BS is blocked while the reflected part is focused onto the sample with the microscope objective. The heart of the microRaman apparatus is the confocal microscope (Olympus BX 40) that allows a high lateral resolution. The objective serves two purposes: (1) to focus the beam on the sample and (2) to collect the backscattered light. The collected back scattered light passes through the beam splitter and then through lens L3 to the adjustable confocal aperture. The confocal aperture “re-defines” the scattering volume, rejecting stray light coming from elsewhere. In effect, the aperture size is chosen to be $M \times 1 \mu$, where $M$ is the magnification given by
Figure 3–7: Schematic of triple grating monochrometer (JY-ISA, T6400) emphasizing the optics of the confocal microscope used to collect Raman spectra of the Nanowires. The objective is the key ingredient (100X aperture, working distance = 1mm) spot size ~ 1.0µ. The confocal aperture is used to redefine the scattering volume and remove spurious or stray light. In effect, the size is chosen to be $M \times 1 \mu$, where $M$ is the optical magnification of the Raman volume produced by the objective in concert with L3.

$$M = f_{L3} f_{obj}^{-1} \quad (3.5)$$

$M$ is the optical magnification of the ~1µ diameter beam spot on the sample produced by the objective in concert with the lens L3. The 1µ spot size is limited by the lateral resolution of the microscope, $f_{L3}$ and $f_{obj}$ are the respective focal lengths of L3 and objective. After the confocal aperture, the Raman scattered light is then focused by the lens L5 onto the entrance slit of the monochrometer (details are shown in Figure 3–8). The light is processed by the subtractive
double monochromator which defines a spectral bandpass as determined by an internal slit width (S2; Figure 3–8). The third grating disperses the spectrum on the CCD detector. Argon ion or Ar-Kr ion lasers were used for excitation. The spectra were collected in air under ambient conditions. Both the vertical and the horizontal polarizations were accepted in the scattered radiation.

**Figure 3–8:** Schematic representation of the T6400 double subtraction premonochromator with spectrograph. The polychromatic radiation enters the first monochromator through entrance slit S1, which determines the instrument resolution. The grating G1 disperses the light and the exit slit S2 selects the bandpass ($\lambda_1 < \lambda < \lambda_2$). In the second monochromator, G2 recombines the dispersed radiation into a polychromatic onto the slit S3. This configuration is used as a tunable filter in the spectral range defined by the scanning mechanism and the gratings. This polychromatic radiation is then dispersed by G3 of the spectrograph. The spectrum is acquired with a liquid nitrogen cooled CCD.
Before any Raman spectra were collected, the spectrometer was calibrated and checked for linearity and repeatability in wavelength and intensity. In this work, a Si wafer (100) was used as a standard sample. The Raman band of crystalline Si at room temperature (300K) occurs at 520.0 ± 0.75 cm\(^{-1}\). To collect Stokes and AntiStokes spectra the gratings must be moved. Therefore, since we are dealing with small changes in position and lineshape, we must determine that these grating rotations do not introduce systematic error, i.e., false shifts in wavenumber. Using the Si first order Raman peak, we find that the instrument is reproducible to ± 0.75 cm\(^{-1}\) even after changing between Stokes and AntiStokes spectra. To check the linearity of the T6400 in wavelength, a spectrum of Si wafer was taken over a larger spectral range: 200 cm\(^{-1}\) to 2000 cm\(^{-1}\) and the 2\(^{nd}\) and 3\(^{rd}\) order peaks (e.g. 520 cm\(^{-1}\) × 2, 520 cm\(^{-1}\) × 3) were found and compared to the expected results. They were found to be in good agreement within ~ 0.75 cm\(^{-1}\), indicating the is linear to within a typical instrumental error. To check the stability in laser intensity and the ability to quantitatively measure the Raman spectrum per incident photon, we acquired Raman spectra of Si wafer with the same accumulation time at various laser fluxes. The intensity of the first order Si Raman peak versus laser power is plotted in Figure 3–9a. The solid circles are the data and the solid line is the least squares fit to the data subject to the condition that its intercept is zero. There is no evidence for a non linearity for laser flux up to 14mW in a 1\(\mu\) focal spot size. This indicates also that the Si wafer at these fluxes behaves in a normal manner (i.e. 1\(^{st}\) order scattering). In Figure 3–9b, we plot the line width versus laser flux. As can be seen from the plot, the linwidth is invariant with laser power up to 14mW which means that there is no broadening in the line shape due to thermal heating. However, Nanowires
can be easily heated by the laser flux at flux ≥ 1mW/μ². This is really important in the current study of the Raman lineshape, and will be discussed in detail later.

In Raman spectroscopy, one always encounters a composite line function which is due to a convolution of the instrumental function and the natural Raman lineshape itself.

\[ I(\omega) = \int_{-\infty}^{\infty} F_1(\omega')F_2(\omega - \omega')d\omega' \]  

(3.6)

The measured spectrum \( I(\omega) \) is given by [7]

The instrument function \( F_2 \) normally has a maximum when \( \omega - \omega' = 0 \) and can be either a Gaussian, a Lorentzian, or a triangular function, whereas the natural lineshape function, \( (F_1) \) can either be a Lorentzian, a Fano, or Fouchet-Campbell function, for example. A special case of the measured function \( I(\omega) \) is a “Voigt” function which is a convolution of a Lorentzian lineshape and a Gaussian instrument function. Traditionally, 1\textsuperscript{st} order peaks exhibits a Lorentzian shape.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure3-9.png}
\caption{a) the linearity and, b) stability of the Raman scattering intensity vs. laser power of the T6400 spectrometer. The sample was a Si (001) wafer}
\end{figure}
The Gaussian function is a reasonable approximation to the instrumental function at a small slits where weak diffraction phenomenon take place. The Gaussian instrument function is given by

\[ I(\omega) = Ae^{\left(-\frac{(\omega-\omega_0)^2}{2\sigma^2}\right)} \quad (3.7) \]

where \(2\sigma^2 = 0.36\Gamma_G\) and \(\Gamma_G\) is the FWHM of the Gaussian function. This function would be the measured response of the spectrometer to a very narrow line much as an atomic line in a low pressure gas lamp (e.g., Neon). The line position is \(\omega_0\). Note that in both equations the functions have been written so that the width parameters reflect the full width at half maximum (FWHM). At wider slits the instrumental function becomes a triangular. The Voigt function is therefore expressed as

\[ V(\omega) = \frac{2\alpha^2}{\pi^{\frac{1}{2}}\gamma_L} \int_{-\infty}^{\infty} \exp\left(-\frac{\mu^2}{\alpha^2}\right) \cdot d\mu \quad (3.8) \]

and

\[ \gamma_L = \frac{1}{\pi\tau}, \quad \alpha = \sqrt{2}\left(\frac{\gamma_L}{\gamma_G}\right) \quad (3.9) \]

\[ \mu = \frac{2\sqrt{\ln 2}\omega}{\gamma_G}, \quad \xi = \frac{2\sqrt{\ln 2}(\omega-\omega_0)}{\gamma_G}, \]

where \(\gamma_L\) and \(\gamma_G\) are the Lorentzian and Gaussian half width at half maximum (HWHM) and where \(\omega_0\) is the peak frequency, \(\tau\) is the scattering life time of the phonon and \(\omega\) is the frequency variable. The proportion of Lorentzian and Gaussian contributions to the Voigt function is sometimes discussed in terms of the Voigt parameter \(a\), defined as
\[ a = \frac{\gamma_L}{\gamma_G} \]  

(3.10)

From equations 2.11, 2.12 and 2.13, it can be seen that when \( \gamma_L \gg \gamma_G \approx a \) Lorentzian \( I(\omega) \) is obtained, and when \( \gamma_L \ll \gamma_G \approx a \) Gaussian \( \gamma_L \sim \gamma_G \) a Voigt function is obtained. The instrumental function for the spectrometer can be measured by observing the shape of a very narrow line, e.g. plasma discharge line from the laser. If we use a Lorentzian natural line shape function of a form

\[
F_1(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - \omega_o)^2 + \Gamma^2} \]  

(3.11)

where \( \Gamma = 2\gamma \) then,

\[
\delta(\omega' - \omega_o) = \lim_{\Gamma \to 0} \frac{1}{\pi} \frac{\Gamma}{(\omega' - \omega_o)^2 + \Gamma^2} \]  

(3.12)

That is, the Lorentzian lineshape is a representation of a delta function in the limit of vanishing natural line width \( \Gamma \), and equation 3.9 becomes

\[
I(\omega) = \int_{-\infty}^{+\infty} F(\omega - \omega')\delta(\omega' - \omega_o)d\omega' \]  

(3.13)

Thus the measured function \( I(\omega) \) is just the instrumental function \( F_2(\omega) \) shifted by \( \omega_o \).

In this work, two separate routes (a Voigt function analysis and Gaussian plasma lineshape analysis) were employed to determine the instrumental broadening of our spectrometer. First, let us consider the Voigt profile analysis. Voigt profile of bulk Si was used to determine the instrumental broadening of the spectrometer. The half width at half maximum (HWHM) of the Voigt function can be expressed as[8-11],
The instrumental broadening for the 520 cm$^{-1}$ line in a standard sample of bulk Si ($\Gamma = 2\gamma = 4.0$ cm$^{-1}$ at 300K [12]) was also measured to confirm the instrumental broadening. Several spectra of the bulk were taken, and the linewidth of each spectrum was measured from a Voigt function (equation 3.15) fit to the lineshape. A fit to one of the profiles is shown in Figure 3–10a. The average, $\Gamma_V$ of the measured linewidths was taken and the instrumental broadening $\Gamma_I = 2\gamma_G$ was calculated using equation 3.17, with FWHM of Si $\Gamma_L = 2\gamma_L = 4$ cm$^{-1}$. The FWHM from the Voigt function fit also $\Gamma_V = 4.5$ cm$^{-1}$ and $a = \Gamma_L/\Gamma_V$. The broadening of the T6400, $\Gamma_1$ was found to be $\sim 1.5$ cm$^{-1}$. As a check of the above analysis, we investigated the line profile of a plasma line of an Argon ion laser. Shown in Figure 3–10b are a Lorentzian and a Gaussian fit to the plasma line at 737 cm$^{-1}$ with respect to the 514.5 excitation line of an Argon ion laser. From the fits, it can be seen that the plasma line is best fitted with the Gaussian. The FWHM of the Gaussian fit in Figure 3–10b is $\sim 1.5$ cm$^{-1}$ in good agreement with the previous estimate from the Voigt analysis of the Si first order Raman band at 520.0 cm$^{-1}$.

$$\gamma_V = \frac{1}{2} \left[ \gamma_L + \sqrt{\gamma_L^2 + 4\gamma_G^2} \right] \quad (3.14)$$
Figure 3–10: a) Fit of a Voigt function to the Raman profile of bulk Si. From the analysis, the instrumental broadening is estimated to be ~1.5 cm. b) comparison of a Gaussian fit and a Lorentzian fit to a plasma line at 737 cm relative to the 514.5 nm Ar ion

### 3.6.2 Spatial Resolution of Raman Microscope

According to the Raleigh diffraction criteria a collimated beam can be focused to a spot on the sample with a minimum diameter given by

\[
d_{sp} = \frac{1.22\lambda}{NA}
\]

where \(\lambda\) is the wavelength of the collimated beam, and \(NA\) is the numerical aperture of the microscope objective. Using equation 3.16 assumes that the aperture of the objective is filled. The numerical aperture of a microscope depends on the solid angle and the refractive index (n) of the material of the lens and is given by
\[ NA = n \sin \alpha , \]  

(3.17)

where \( \alpha \) is the half-angle of the solid angle of the light from the objective lens.

Using a X100 objective with \( NA = 0.95 \), the spot size in the sample should be \( \sim 0.661\mu \).

However, the instrument is rated at \( \sim 1\mu \) lateral resolution.
REFERENCES


Chapter 4
Raman Scattering from Elemental Semiconductors

4.1 Introduction

In this chapter, we discuss the theoretical background behind Raman Scattering in elemental Si and Ge. We consider how disorder, temperature, phonon confinement (size effect) and interference scattering between conduction electrons and phonons all affect the Raman spectrum of Si and Ge. In the subsequent chapters, we present our experimental data on Si and Ge nanowires and consider which of these phenomena (disorder, interference scattering, etc.) are consistent with our results.

Raman Scattering Spectroscopy has been used extensively to study many physical properties of bulk semiconductors [1-3]. For example, in addition to the traditional use of obtaining the optical mode frequencies and symmetries at $q = 0$ and the phonon frequencies at various points in the Brillouin zone from second order scattering, Raman scattering has also been shown to be useful for determining free carrier concentration [4-8], electron mobility [8, 9], phonon lifetime [10], resistivity [11, 12], alloy composition [10, 13], crystallinity [14], stress [10, 13], the presence of impurities [4] and defects [15-18]. A series of research monographs on Raman scattering in semiconductors (edited by Cardona and others) [3] have been published over the past three decades and contains a large body of useful information for this thesis.
In very small size semiconductor systems, e.g., nanostructures (quantum dot, nanowires and clusters) the phonon states and the Raman selection rules can be significantly different from those of the bulk. One speaks of “phonon confinement” phenomena as changes in the observable phonon properties due to the small size of the system. Long range interactions between atoms are also lost for many of the atoms in the system (particularly those near the surface), and theoretical calculations are needed to deal with the effect of the sample surface boundary. In this chapter, we will consider a continuum model that describes the impact of phonon confinement on the Raman spectrum. It is expected that the spectrum of the nanostructure will be different from that of the bulk, and that this difference will increase as the system gets smaller.

### 4.2 Phonons in Si and Ge

Both Germanium and Silicon belong to the cubic $O_h^7$ space group and crystallize in the (F4$_1$/d32/m) diamond lattice. The conventional lattice of diamond consists of two interpenetrating face-centered cubic (fcc) atomic lattices which are displaced a quarter of the body diagonal of the conventional cubic cell with respect to each other. Each atom is tetrahedrally bonded to four nearest neighbors. The unit cell is shown in Figure 4–1 (i) and the corresponding Brillouin zone showing the positions of several high-symmetry axes ($X$, $L$, $W$, $K$) and points ($\Gamma$, $\Lambda$, $\Delta$, $\Sigma$) is shown in Figure 4–1 (ii) [19]. The phonon dispersion curves along some of these high-symmetry directions for crystalline Si and Ge obtained from neutron scattering data [20, 21] (dots) and a fit to the data using up to the sixth nearest neighbor in the Born-von Kármán force constant model (solid line) are shown in Figure 4–2 [22]. At the points...
in the Brillouin zone where the phonon dispersion curves flatten, $d\omega/dk \sim 0$, and peaks appear in the one phonon density of states (pdos). However, in highly disordered systems, these features in the phonon density of states are observed to be broadened. Shown in Figure 4–3 are the calculated one phonon density of states for bulk crystalline Ge and Si. The dashed and solid lines represent, respectively, pdos for the crystalline and highly disordered systems [23]. Note that disorder introduces both a smearing of the sharp peaks in the pdos and a disappearance of the fine structures associated with the crystalline state. However, ~3 broad pdos features remain. Interestingly, strong disorder does not destroy the main features of the phonon density of states associated with the crystalline state.

Figure 4–1: (i) Conventional cubic unit cell for the diamond crystal structure (F41/d32/m). Each atom is tetrahedrally bonded to four nearest neighbors. The lattice parameter of the conventional unit cell containing four atoms, $a = 0.5431$ Å (Si) and $a = 0.5658$ Å (Ge). The primitive cell contains two atoms, therefore three optical branches (2TO and 1LO) and thee acoustic branches (2TO and 1LO) are observed, and (ii) Brillouin zone for the face-centered space lattice showing the positions of several high-symmetry axes and points [24,25]
Figure 4–2: Phonon dispersion curves of Ge [22] (left) and Si [22] (right) along high symmetry directions. The dots are neutron scattering data [20, 21, 24] and the solid lines are from the calculations by Wang and coworkers using up to the sixth nearest neighbor interactions in a Born-von Kármán force constant model [22].

Figure 4–3: Calculated phonon density of state for Si (left) and Ge (right). Solid lines represent a highly disordered material and the dashed line represent the crystalline material [23].
If one compares the 1\textsuperscript{st} order Raman spectrum for disordered and crystalline Si (for example), one observes at room temperature a sharp Lorentzian line at $\sim 520 \text{ cm}^{-1}$ of FWHM $\sim 4 \text{ cm}^{-1}$ for the crystalline state. Strongly disordered Si exhibits a Raman spectrum that approaches the calculated one-phonon density of states (Figure 4–4). In this case, the peak at $\sim 520 \text{cm}^{-1}$ now exhibits a FWHM $\sim 100 \text{ cm}^{-1}$, that is $\sim 25$ times broader than the crystalline bulk. In Figure 4–4, the calculated one phonon density of states (thin solid line), Raman spectrum (thick solid line) and calculated Raman spectrum (dashed line) of a highly disordered Si are compared. It can be seen that the experimental and the calculated Raman data are in reasonably good agreement.

*Figure 4–4*: Comparison of the calculated pdos (thin solid line) and the calculated first-order Raman band of highly disordered Si (dashed line). The bold solid line is the measured Raman spectrum for highly disordered Si. The experiment and calculated Raman spectra are seen to be in good agreement. The difference in the pdos and the calculated Raman band shows the importance of matrix element effects. Both the pdos and the Raman spectrum have similar structures in their band profile: three distinct peaks of FWHM $\sim 100 \text{ cm}^{-1}$ can be observed and identified with the pdos at the zone center and the zone edge, consistent with the phonon dispersion curve of Figure 4–2.

Also it can be seen that matrix element effects are important if a truly quantitative analysis of the data is desired. Nevertheless, the Raman spectrum of highly disordered system can provide very important phonon density of states information throughout the entire frequency range.
4.3 Theory of Raman Scattering in Crystalline bulk semiconductor systems

The narrow 520 cm\(^{-1}\) Lorentzian line observed in first order Raman scattering from crystalline Si is a direct consequence of the crystal momentum selection rule. In Raman scattering, the Stokes and Antistokes radiation processes are schematically illustrated in Figure 4–5. The Stokes process is a phonon or vibration creation process, and the incoming photon deposits energy in the system. In the AntiStokes process, a phonon or vibration quantum is annihilated and contributes energy to the scattered photon. Indicated in Figure 4–5 are the electronic ground and excited states, the vibration states are simply indicated by a 0 or 1. That is \(|k_o,1\rangle\) refers to a one phonon excitation with the system in the electronic ground state. The system starts and finishes in the electronic ground state. The electric field of the incident photon drives transitions between the ground state and the excited electronic state. Only one excited electronic state is shown together with the associated vibration states. To get an accurate answer for the scattering rate, one must consider the transitions to all possible excited electronic states. It is only in resonant Raman scattering that one can focus on the principal electric dipole transition resonating with the laser. The Feynman diagram for a Raman scattering from semiconductors is shown in Figure 4–6 and the corresponding crystal momentum conservation for q00, forward and backward scattering are shown in Figure 4–7.

The Raman effect in crystals can be described by a third order perturbation theory [26]. The transition rate, \(R\), of a Raman Scattering process between the initial state \(|\Psi_i\rangle\) and final state \(|\Psi_f\rangle\) is given by Fermi’s Golden Rule, [26-28]
\[ R_i = \frac{2\pi}{\hbar} |T_{ij}|^2 \delta\left(E_f - E_i \pm \hbar \omega_p\right) \quad (4.1) \]

**Figure 4–5**: Schematic illustration of the energy conservation in a Raman Scattering process indicating the initial state and the final state of the Stokes scattering process (phonon creation) and the AntiStokes scattering process (phonon annihilation).
Figure 4–6: Schematic scattering event, and the corresponding Feynman diagrams for Raman scattering process in a semiconductor. a) and b) show the formation of the electron-hole pair in the scattering process, e and h denotes electrons and holes, respectively, and the numbers show the order of the electronic transitions.
Figure 4–7: Schematic representation of momentum conservation in Raman Scattering involving
the emission of a phonon of wave vector $q$. The photon wave vectors $k_i$ and $k_s$ for the incident
and the scattered light. $\theta$ is the scattering angle, i.e., the angle between $k_i$ and $k_s$. a) is the general
case, (b), (c) and (d) refer, respectively, to forward scattering, right angle scattering and
backscattering. In opaque solids only (d) is possible because the scattering photon will be
absorbed in the scattering volume. It can be seen that $\Delta k = \bar{k}_s - \bar{k}_i = \bar{q}$ and, further, more,
that $|\bar{q}| \leq |\bar{k}_i|$. Therefore, for $k_i = 2 \pi \lambda_{\text{visible}}^{-1}$, $|k_i| \ll \frac{\lambda}{\bar{q}}$, which is the longest wave vector in the
Brillouin zone.
where the matrix element $T_{ji}$ is given by the expression [26-28]

$$T_{ji} = \left(\frac{e}{m}\right)^2 \sum_{\nu,\alpha} \sum_{\sigma,\rho} \left\{ \frac{\langle \Psi_f \mid H_{ep} \mid \Psi_\alpha \rangle \langle \Psi_\alpha \mid \bar{A}_\sigma \cdot \bar{p}_\sigma \mid \Psi_i \rangle \langle \Psi_i \mid \bar{A}_\rho \cdot \bar{p}_\rho \mid \Psi_v \rangle}{(E_\alpha - E_i)(E_v - E_i)} \right\}$$

$$+ \left\{ \frac{\langle \Psi_f \mid \bar{A}_\sigma \cdot \bar{p}_\sigma \mid \Psi_\alpha \rangle \langle \Psi_\alpha \mid H_{ep} \mid \Psi_v \rangle \langle \Psi_v \mid \bar{A}_\rho \cdot \bar{p}_\rho \mid \Psi_i \rangle}{(E_\alpha - E_i)(E_v - E_i)} \right\}$$

$$+ \left\{ \frac{\langle \Psi_f \mid \bar{A}_\sigma \cdot \bar{p}_\sigma \mid \Psi_\alpha \rangle \langle \Psi_\alpha \mid \bar{A}_\rho \cdot \bar{p}_\rho \mid \Psi_i \rangle \langle \Psi_i \mid H_{ep} \mid \Psi_v \rangle}{(E_\alpha - E_i)(E_v - E_i)} \right\} \quad (4.2)$$

$H_{ep}$ is the Hamiltonian for the electron-phonon interaction given by [26-28]

$$H_{ep} = \sum \frac{\partial U}{\partial \bar{Q}} \cdot \bar{Q} \quad (4.3)$$

and

$$H_{\sigma} = \frac{e}{m} \sum \bar{A} \cdot \bar{p} \quad (4.4)$$

is the Hamiltonian representing the interaction between the electron and the electromagnetic field of the incident or scattered photon. $\bar{A}$ is the vector potential of a particular photon and $\bar{p}$ is the electron momentum operator. The summation over $\nu$ and $\alpha$ covers all possible intermediate states, while the summation over $\rho$ and $\sigma$ extends over all the electronic coordinates. $U$ is the lattice deformation potential. The interaction processes described by the matrix elements, in equation 4.2 can be represented by the Feynman diagrams shown in Figure 4–8. The first factor in equation 4.2 is represented by Figure 4–8a and b. In Figure 4–8a, the incident photon $\bar{k}_i$ is absorbed at the first vertex, and the scattered photon $\bar{k}_s$ is emitted at the second vertex, and the
phonon $\vec{q}$ is emitted at the third vertex. In *Figure 4–8b* the order of absorption and the emission photons is reversed.

*Figure 4–8*: Feynman diagrams of a Stokes Raman process (equation 4.2) in a crystal. (a) the incident photon is absorbed at the first vertex, the phonon is emitted at the second vertex, and the scattered photon is emitted at the third vertex. (b) the order of emission and absorption of the incident and scattered photons is reversed. In (c) and (d), the process is the same as (a) and (b), respectively, except that the phonon is now emitted at the second vertex. The same process is repeated in (e) and (f) except the phonon is emitted at the first vertex. (i), (ii) and (iii) refer to terms (1), (2) and (3) on the right side of equation 4.2 respectively.

The second term in equation 4.2 is illustrated by *Figure 4–8c* and *d* with the processes in *Figure 4–8a* and *b* repeated respectively, except that the phonon is now emitted at the second vertex. The last factor in equation 4.2 is represented by the *Figure 4–8e* and *f* and the process in *Figure 4–8a* and *b* is repeated, except that the phonon is emitted at the first vertex.
vertex. The interchange of the order of photon emission or absorption happens because the
vector potential \( \tilde{A} \) contains photon creation, as well as annihilation, operators.

Let us consider the implications of the matrix element appearing in equation 4.2. These
will determine the Raman selection rules. The operator \( \tilde{A} \) can either absorb or emit a photon.
Let us first consider the matrix element \( \langle \Psi_v | \tilde{A}_\rho \cdot \tilde{p}_\rho | \Psi_i \rangle \), considering only the absorbed process.

The vector operator \( \tilde{A} \) can be written as

\[
\tilde{A}_\rho = \sqrt{\frac{\hbar}{2e_p \omega_p V}} \tilde{e} \left( b^+ e^{-i \beta_p \cdot \vec{r}} + be^{i \beta_p \cdot \vec{r}} \right),
\]

(4.5)

where \( b^+ \) and \( b \) are the creation and annihilation operators, \( \tilde{e} \) is the polarization vector, \( \tilde{\beta} \) is the
wave vector of the incident wave, and \( \omega_p \) is the frequency. If the initial state is written as

\[
|\Psi_i\rangle = |n_{p_i}, n_{p_r}\rangle \prod_k |0\rangle \left\{ \psi_{01}, \psi_{02}, \ldots, \psi_{0J} \right\},
\]

(4.6)

where the state vectors \( |n_{p_i}\rangle \) and \( |n_{p_r}\rangle \) describe the incident and the scattering states,
respectively, \( |0\rangle \) are all the phonon states and the electron state vector \( |\psi_{01}, \psi_{02}, \ldots, \psi_{0J}\rangle \)
describes the ground state of the \( J \) electrons. The electrons states can be described by the Bloch
function given by

\[
\psi_i(x_j) = e^{i \hat{\beta}_p \cdot \vec{r}} u_i(x_j)
\]

(4.7)

Thus from equations 4.4 to 4.7 [26]

\[
\langle \Psi_v | \tilde{A}_\rho \cdot \tilde{p} | \Psi_i \rangle \propto -\frac{i \hbar}{\Delta} \int \left\{ i \left( \tilde{e} \cdot \tilde{k}_{oj} \right) u^*_j u_{oj} + u^*_j \tilde{e} \cdot \nabla u_{oj} \right\} d^3x \times \frac{1}{\Delta} \int e^{i (k_{oj} + \rho_p \cdot \vec{r})} d^3x
\]

(4.8)

The last integral in equation 4.8 is zero unless
\[ \vec{k}_{ij} - \vec{k}_{vj} + \beta_{p_i} = 0 . \quad (4.9) \]

Similar evaluation of \( \langle \Psi_{\alpha} | \vec{A}_{\sigma} \cdot \vec{p} | \Psi^\prime \rangle \) and \( \langle \Psi_f | H_{\alpha \sigma} | \Psi_{\alpha} \rangle \) in equation 4.2 leads to the conditions

\[ \vec{k}_{sk} - \vec{k}_{ak} - \beta_{p_s} = 0 \quad (4.10) \]

and

\[ \vec{k}_{ak} - \vec{k}_{\mu ak} + \vec{k}_{\sigma al} - k_{\mu sj} - \gamma_{p_s} = 0 , \quad (4.11) \]

respectively. Thus, for any of the six Raman scattering process as shown in Figure 4-8 where a phonon is created (Stokes), it is required that [26]

\[ \left( \vec{p}_{p_s} - \vec{p}_{p_s} - \vec{v}_{p_s} \right) + \left( \vec{k}_{oj} - \vec{k}_{vj} + \vec{k}_{sk} - \vec{k}_{ak} + \vec{k}_{\sigma ak} - \vec{k}_{\mu ak} + \vec{k}_{\sigma al} - \vec{k}_{\mu sj} \right) = 0 \quad (4.12) \]

However,

\[ \mu_{ak} = \alpha k , \quad \mu_{oj} = \sigma j , \quad \text{or} \quad \mu_{ak} = \sigma k , \quad \mu_{oj} = \sigma j \quad \text{and} \]

\[ \sigma_{ak} = \alpha k , \quad \sigma_{vj} = \nu f , \quad \text{or} \quad \sigma_{ak} = \nu f , \quad \sigma_{vf} = \alpha k . \quad (4.13) \]

And the net electronic contribution to the scattering process is zero, leaving

\[ \beta_{p_s} - \beta_{p_s} - \gamma_{p_s} = 0 \quad (4.14) \]

Equation 4.14 is the wave vector conservation for a Stokes (phonon creation) process. Each term in equation 4.2 can generate this selection rule. Similarly, we can show that for an AntiStokes process we must have

\[ \beta_{p_s} - \beta_{p_s} + \gamma_{p_s} = 0 . \quad (4.15) \]

From equation 4.1, the energy delta function requires that

\[ E_f - E_i \pm \hbar \omega_{p_s} = 0 , \quad (4.16) \]

or
\[ h\omega_{p_i} - h\omega_{p_j} \pm h\omega_{p_k} = 0, \]  

(4.17)

which is the energy conservation rule in a Raman Scattering process. The ± refers to Stokes or AntiStokes processes. In a Raman scattering experiment, the geometry of the scattering experiment determines the magnitude and orientation of the scattering wave vector. The scattering wave vector \( q \) has a minimum magnitude in a forward (i.e., \( \theta = 0^\circ \)) scattering configuration and a maximum value in the backscattering geometry (i.e., \( \theta = 180^\circ \)) as illustrated in Figure 4–7, i.e.

\[ k_i - k_s < |q| < k_i + k_s, \]  

(4.18)

In a typical Raman Scattering experiment with visible light (\( \lambda \sim 400\text{nm–800nm} \)), \(|k_{\text{max}}| \leq 10^6 \text{ cm}^{-1} \), which is about two orders of magnitude smaller than the zone boundary wave vector (\( \pi/a \)) for a typical crystal where \( a \) is the lattice constant. Thus in a first order Raman scattering processes, where wave vector conservation is observed, only phonons with \( q \approx 0 \) (zone center) participate in the scattering process.

However, in disordered systems, there is a perturbation in the periodicity of the crystal structure which destroys the crystal momentum as a variable, and the wave vector selection rule is lost. However, energy must still be conserved, so the energy delta function in equation 4.1 still holds for the Raman process. In sufficiently small structures, quantum confinement effects can be anticipated. We will show that they also cause a breakdown of the wave vector selection rule. In this case, the reason is not loss of crystallinity, but the fact that the phonon states in the small system cannot be described by a single bulk phonon wave vector. In fact, the confinement
implies that a nanowire phonon must be described as a linear combination of infinite crystal
\( \tilde{q} \) phonon states. This will be described in detail later.

### 4.4 Raman Selection rule in Crystalline Si and Ge

A Raman active process depends on the polarization directions of the incident and the scattered light and the Raman tensor. In the first order Stokes Raman effect, an incident photon of frequency \( \omega_i \) is absorbed, a scattered photon of frequency \( \omega_s \) is emitted along with a long wavelength lattice vibration (optical phonon) of frequency, \( \omega_i - \omega_s \). From equations (4.1), (4.4) and if the lattice displacement is expressed as [26]

\[
Q_\sigma = \sum_\sigma Q_\sigma \left\{ b_\sigma^+ e^{-i\tilde{q}_\sigma \cdot \tilde{r}_\sigma} + b_\sigma e^{i\tilde{q}_\sigma \cdot \tilde{r}_\sigma} \right\}, \tag{4.19}
\]

then the scattering efficiency defined as the Raman cross section per unit volume, i.e., the radiative energy at frequency \( \omega_s \) scattered into a solid angle \( d\Omega \) in a unit volume of crystal and in unit time, divided by the energy flux of the incident radiation, is given by [29, 30]

\[
\frac{d\sigma^2}{d\Omega d\omega} \propto \left( \frac{e}{c} \right)^4 \left( \frac{\omega_s}{\omega_i} \right)^4 \left| \hat{e}_s \cdot R_{i_1}^m \cdot \hat{e}_i \right|^2 (n+1) \tag{4.20}
\]

where \( \omega_i \) and \( \omega_s \) are the frequencies of the incident and the scattered light respectively, \( \hat{e}_i \) and \( \hat{e}_s \) are the respective polarization unit vectors and the second rank tensor \( R_{ij}^m \) is the first order Raman tensor, given by [29, 30]
\[
\begin{align*}
R^k = & \frac{1}{V} \sum_{\alpha,v} \left\{ \frac{p^i \Pi^i_{\alpha} \Pi^{j}_{\alpha}}{(\omega_v + \omega_{op} - \omega_j)(\omega_{op} + \omega_j)} + \frac{p^j \Pi^j_{\alpha} \Pi^{i}_{\alpha}}{(\omega_v + \omega_{op} + \omega_S)(\omega_{op} + \omega_j)} \\
& + \frac{p^j \Pi^j_{\alpha} \Pi^{i}_{\alpha}}{(\omega_v + \omega_{op} - \omega_j)(\omega_{op} + \omega_j)} + \frac{p^i \Pi^i_{\alpha} \Pi^{j}_{\alpha}}{(\omega_v + \omega_{op} + \omega_S)(\omega_{op} + \omega_j)} \right\} \quad (4.21) \\
& \left\{ \frac{\Pi^k_{\alpha} p^j p^i_{\alpha}}{(\omega_v + \omega_{op} - \omega_j)(\omega_{op} + \omega_j)} + \frac{\Pi^k_{\alpha} p^j p^i_{\alpha}}{(\omega_v + \omega_{op} + \omega_S)(\omega_{op} + \omega_j)} \right\}
\end{align*}
\]

where the matrix element \( \Pi \) is from the deformation potential in equation 4.3. The above expressions do not take into accounts any damping effects. The most important damping effect in the Raman scattering process of intrinsic semiconductors comes from anharmonic phonon interactions, which modifies the above expression to [29, 30]

\[
\frac{d\sigma^2}{d\Omega d\omega} \propto \left( \frac{e}{c} \right)^4 \left( \frac{\omega_S}{\omega_f} \right) |\vec{e}_{S_i} \cdot R_{ij,k}\vec{e}_{f_j}|^2 \left( n + 1 \right) \left( \frac{1}{(\omega_f - \omega_{op} - \omega_S - \Delta)^2 + \Gamma^2} \right) \quad (4.22)
\]

where \( \Gamma \) is the inverse lifetime of the long wave optic phonon and is given by

\[
\Gamma \propto \sum_{av} dq \langle \Psi_f | H_A | \Psi_i \rangle^2 \delta(\omega_{op} - \omega_{aq} - \omega_{v-q}) \quad (4.23)
\]

and

\[
\Delta \propto P \sum_{av} dq \sum_{av} \frac{\langle \Psi_f | H_A | \Psi_i \rangle^2}{\omega_{op} - \omega_{aq} - \omega_{v-q}} \quad (4.24)
\]

\( H_A \) is the Hamiltonian of the anharmonic interaction and \( P \) means principal value. The matrix elements in equation 4.23 and 4.24 represent processes where the \( q = 0 \) optic phonon is destroyed and two acoustic phonons of equal and opposite wave vectors are created. The expression in equation 4.22 shows that the Raman scattered radiation has a Lorentzian profile about the frequency \( \omega_f - \omega_{op} - \Delta \) with half width \( \Gamma \). Equation 4.22 can be written in a simple form as:
It is well known from the semi-classical treatment of inelastic light scattering that the Raman scattering efficiency is proportional to \( \omega_s^3 \omega_L \). However, from the quantum mechanical treatment, the scattering efficiency varies as \( \omega_s / \omega_L \). Cardona and coworkers [31] and Loudon [32] have separately shown that both statements are consistent and have developed a transformation through the use of the Raman tensor to show the consistency of both pre-factors in the scattering process.

From the above equations, it can be seen that a key feature in the Raman scattering process is its dependence on the incident and the scattering polarization vectors and the symmetry of the Raman tensor. Since the scattering cross section is a scalar, it is invariant under any of the symmetry operations of the crystal and thus could be written simply as [32]

\[
\frac{d\sigma^2}{d\Omega d\omega} \propto A \left| \sum_y R_{y,k} \vec{e}_y \cdot \vec{Q}_k \right|^2
\]  

(4.26)

where \( A \) is a constant of proportionality. For two-, or three-fold degenerate phonons, the contributions of the two or three matrices must be added to find the total scattering cross section. As an example, consider the scattering geometry shown in Figure 4–9, for an F\(_{2g}\) vibration (using the standard notation for the O\(_h\) group), the Raman efficiency for a scattered light polarized in the scattering plane (i.e., xz-plane) is [32]

\[
S_\parallel = Ad^2 \left[ (e_x^s \sin \psi)^2 + (e_y^s)^2 \right]
\]

\[
S_\perp = Ad^2 (e_x^s)^2.
\]  

(4.27)
When \( \psi = \pi/2 \), the sum of \( S_\parallel \) and \( S_\perp \) contains the three terms of the Raman tensor along \( xyz \). Also, since the right hand side of equation 4.26 must also be invariant, it implies that \( e_i e_j Q_k \) must also be invariant under the symmetry properties of the crystal.

![Figure 4–9: Schematic representation of a backscattering geometry in \( x(yz)\bar{x} \) configuration where \( k_s \) and \( k_i \) are the scattered and the incident wave vectors and \( e_s \) and \( e_i \) are the corresponding polarizations. The plane of incidence is (100).](image)

The irreducible representations of the \( O_h \) point group are listed in Table 4–1 with some of the corresponding basis functions. The product \( e_i e_j \) transforms in the same way as a quadratic polynomial. Thus optical phonons that belong to irreducible representations with quadratic polynomials as their basis function will be Raman-active.
Table 4–1: \( O_h \) point group irreducible representation

<table>
<thead>
<tr>
<th>Irreducible Representation</th>
<th>Polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1(A_{1g}) )</td>
<td>( x^2 + y^2 + z^2 )</td>
</tr>
<tr>
<td>( \Gamma_1'(A_{1u}) )</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_2(A_{2g}) )</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_2'(A_{2u}) )</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_{12}(E_g) )</td>
<td>( \begin{bmatrix} \sqrt{3}(x^2 - y^2), &amp; 2z^2 - x^2 - y^2 \end{bmatrix} )</td>
</tr>
<tr>
<td>( \Gamma_{12}'(E_u) )</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_{15}(F_{1u}) )</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_{15}'(F_{1u}) )</td>
<td>( \begin{bmatrix} x(z^2 + y^2), &amp; y(z^2 + x^2) \end{bmatrix} )</td>
</tr>
<tr>
<td>( \Gamma_{25}(F_{2g}) )</td>
<td>( \begin{bmatrix} yz, xz, xy \end{bmatrix}, \begin{bmatrix} yz^2, xz^2, xz^2 \end{bmatrix} )</td>
</tr>
<tr>
<td>( \Gamma_{25}'(F_{2u}) )</td>
<td>( \begin{bmatrix} x(y^2 - z^2), &amp; y(z^2 - x^2), &amp; z(x^2 - y^2) \end{bmatrix} )</td>
</tr>
</tbody>
</table>

From Table 4.1, only \( A_{1g}, E_g \) and \( F_{2g} \) are Raman-active. Since \( \{Q_x, Q_y, Q_z\} \) and the polynomial \( \{yz, xz, xy\} \) are both basis functions for the same representation, from Unsöld’s theorem, it implies that:
\[ Q_x e_y e_z + Q_y e_z e_y + Q_z e_x e_y = \text{invariant} \quad (4.28) \]

Only one such combination can be formed, implying that the Raman tensor has the form shown in equation 4.29 and corresponds to phonon eigenvectors along the \( x, y \) and \( z \) axes, respectively.

\[
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & a \\
0 & a & 0
\end{pmatrix}
\begin{pmatrix}
0 & a & 0 \\
0 & 0 & 0 \\
a & 0 & 0
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 0 \\
a & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

\( (4.29) \)

Since the three optical phonons in Si or Ge are degenerate, any linear combination of these eigenvectors can also be chosen as eigenvector. The Raman tensors (equation 4.29) impose polarization selection rules. The tensor specifies that, in a coordinate system aligned with the crystal axis, Raman scattering is allowed when the incident and the scattered polarization are orthogonal to the phonon displacement coordinates \( (Q_k) \). For instance, in a \( R_{ij,x} \) mode, the polarizations are perpendicular to each other and lie in the \( y-z \) plane (Figure 4–9). A short hand notation: \( x(yz)\bar{r} \) is often used to represent backscattering from a (100) surface. Where, the first and the last terms indicate the incident and the scattered directions, respectively. The second and the third entries indicate the polarization directions.

### 4.5 Determination of Sample Temperature by Raman Spectroscopy

For a Stokes Raman process in the backscattering configuration and in a strongly absorbing system, the energy in the scattered radiation produced per unit time and unit
cross-sectional area must depend on the both scattering efficiency and the optical absorption coefficients. In this case the scattered intensity is given by [30]:

\[
I_s \propto \left( \frac{\omega_s}{\omega_i} \right)^3 \left( \frac{1}{\alpha_i + \alpha_s} \right) S(\omega_i, \omega_s) [n(\omega) + 1]. \tag{4.30}
\]

It is well known that the ratio of the intensities of Stokes and AntiStokes scattering is proportional to temperature in the scattering volume. The Stokes and the AntiStokes Raman process correspond, respectively, to the emission and absorption of phonon. The ratio of their intensities can therefore be expressed as [33]:

\[
\frac{I_s}{I_{AS}} = \frac{\alpha_i + \alpha_{AS}}{\alpha_i + \alpha_S} \left( \frac{\omega_s}{\omega_{AS}} \right)^3 \left( \frac{S(\omega_i, \omega_s)}{S(\omega_i, \omega_{AS})} \right) \frac{n_o(\omega_o) + 1}{n_o(\omega_o)}, \tag{4.31}
\]

where \(I_s\) and \(I_{AS}\) are respectively the intensity of the Stokes and AntiStoke Raman radiation, \(\alpha_i, \alpha_{AS}, \alpha_S\) are the optical absorption constants at the frequencies \(\omega_i, \omega_{AS}, \omega_s\) (incident, beam Antistokes, and Stokes), \(S(\omega_i, \omega_{AS})\) and \(S(\omega_i, \omega_s)\) are the Raman cross sections at the respective frequencies, and \(n_o(\omega_o)\) is the equilibrium occupation number of the \(q = 0\) optical phonons of frequency \(\omega_o\) given by

\[
n_o = \left[ \exp(\hbar \omega_o / k_B T) - 1 \right]^{-1} \tag{4.32}
\]

Equation 4.31 can be simplified to

\[
\frac{I_s}{I_{AS}} \sim A \exp(\hbar \omega_o / k_B T) \tag{4.33}
\]

where \(T\) is absolute temperature, \(k_B\) is Boltzman’s constant and \(A\) is a normalization parameter which depends on the scattering cross section, optical absorption constant and the Raleigh factor at the Stokes and Antistokes frequencies. The temperature \(T\) can be determined if \(A\) is known. In
this work, $A$ was determined from the Stokes and AntiStoke Raman radiation of a Si wafer (001) at 300K. The intensity ratio was determined from the Raman bands and $A$ was determined using the expression,

$$\ln A = \ln \left( \frac{I_S}{I_{AS}} \right) - \frac{\hbar \omega_c}{k_B T} \quad (4.34)$$

since all other parameters are known. In this work, this technique is used to determine the sample temperature.

### 4.6 Phonon Confinement Model

Electronic and phonon quantum size effects in semiconductors have been the subject of extensive studies in the past decade. The electronic quantum size effect is mostly detected as a shift of the interband absorption or luminescence peak to higher energies. This is normally observed in quantum wells, quantum wires or in quantum dots. However, in this thesis we focus on size-induced phonon confinement effects and we have studied them experimentally via Raman scattering experiments in Ge and Si nanowires.

#### 4.6.1 Phonon Confinement

Richter and coworkers [34] were the first to propose a phenomenological phonon confinement model to explain the experimental observation of a down shift and asymmetrical broadening of the 1$^{st}$ order Raman line in crystalline nanostructures. Their approach naturally leads to a relaxation of the conservation of the bulk crystal momentum in the scattering process.
Assuming a spherical nano-crystallite size, and using the diameter as an adjustable parameter, they fitted the Raman line shape of the film of small Si nanocrystals. Their model was further extended by Campbell and Fauchet [35] who considered other different nanocrystallite shapes (i.e., wires and platelets).

In this work, we applied Richter’s phonon confinement effect model to Si and Ge nanowires, where we have used the experimentally determined nanowire diameter distribution. We have found that the experimental lineshape is laser power dependent and that phonon confinement is one factor that contributes to the lineshape asymmetry.

4.6.1.1 Phonon Confinement in Si and Ge Nanowires

The LO and the TO modes in both Si and Ge are degenerate at the Γ point (zone center). The conservation of the phonon momentum in crystalline Si and Ge produces a Raman active mode of the optical phonons from only the zone center \( q = 0 \) at 520 cm\(^{-1}\) (Si) and 300 cm\(^{-1}\) (Ge). In nanowires, the phonons are confined in the two orthogonal directions perpendicular to the wire axis which is usually the <111> direction. This allows a greater range of phonon modes to contribute to the Raman Scattering process. In fact bulk phonons of wave vector up to \( q \sim 1/2r_o \) contribute to the 1\(^{st}\) order Raman spectrum, where \( r_o \) is the wire radius. The basic points of Richter’s derivation for Raman scattering, from a confined crystalline system are reproduced below [34]

The wave function of a phonon with wave vector \( q_o \) in an infinite crystal (bulk crystal) is given by the Bloch wave function as [34-36]:

\[ \psi(\mathbf{q}) = e^{i\mathbf{q}\cdot\mathbf{r}} \Psi(\mathbf{r}) \]
where $u(q, r)$ has the periodicity of the lattice. Due to the relaxation of the $q = 0$ selection rule as a result of the transverse confinement of the phonons in the nanowires, the phonon wave function of the nanowires $[\Psi_{NW}(q_o, r)]$ are expressed as [34, 35]:

$$
\Psi_{NW}(q_o, r) = W(r, r_o) \Phi (q_o, r)
$$

(4.36)

where $W(r, r_o)$ is a “localization” function that acts as an envelope function truncating the phonon amplitude outside the wire radius $r_o$. For simplicity, Richter chooses the form:

$$
W(r, r_o) = \exp\left[-\gamma \left(r/r_o\right)^2\right].
$$

(4.37)

$\gamma$ is a dimensionless constant. The Gaussian localization function is used as an Ansatz. To calculate the effect on the Raman spectrum, $\Psi_{NW}$ is expanded in a Fourier series at $q_o$ as [34, 35]

$$
\Psi'(q_o, r) = \int C(q_o, q)e^{iq_o \cdot r}d^3q
$$

(4.38)

The Fourier coefficient, $C(q_o, q)$ of the localization function $W(r, r_o)$ is given by the expression [34, 35]

$$
C(q_o, q) = \frac{1}{(2\pi)^{3}} \int \Psi'(q_o, r)e^{-iq \cdot q}d^3q.
$$

(4.39)

The phonon wave function of the nanowire is then seen to be a superposition of the bulk phonon functions with $q$ wave vectors centered at $q_o$. In our case, $q_o = 0$, for the zone center optical phonon. The Fourier coefficients are then given by
\[ |C(0,q)|^2 \equiv \exp[-\beta(q^2 r_o^2)], \quad (4.40) \]

and the intensity of the first order Raman spectrum of the spatially confined phonons in the nanowires can be written as [34, 35, 37-39]:

\[
I_{NW}(\omega, r_o) \equiv \int_{q=0}^{1} \left| \frac{C(0,q)}{\omega - \omega(q)} \right|^2 dq^3 \quad (4.41)\]

where \( \beta \) is a dimensionless constant, \( q \) (expressed in units of \((\pi/a)\)) and \( \Gamma \) is the inverse phonon lifetime. The dispersion relation of the LO optical phonon branch in Si or Ge can be expressed as: [36, 38, 39]

\[
\omega(q) = \left[ A + B \cos\left(\frac{\pi q}{2}\right) \right]^{1/2} \quad (4.42)\]

where \( A \) and \( B \) are constants determined by fitting the neutron scattering data. For an isolated single Ge or Si nanowire, the above phenomenological equation in (4.41) describes an asymmetric Raman line shape. In the limit \( r_o \to \infty \), equation (4.41) reduces to a Lorentzian lineshape:

\[
I \propto \frac{1}{(\omega - \omega(0))^2 + (\Gamma/2)^2} \quad (4.43)\]

characteristic of the infinite system. Shown in Figure 4-10 are plots of equation 4.41 as a function of \( d = 2r_o \) for Silicon nanowires. As can be seen from the figure, the downshift in peak position and the asymmetric broadening to lower energy, increase with decreasing diameter of the nanowire. Also shown is the Lorentzian lineshape of the bulk (equation 4.43) for comparison. It is assumed that \( \Gamma \) does not exhibit a significant dependence on \( r_o \).
Figure 4–10: A plot of equation 4.41 showing the finite size induced phonon confinement effect (downshift and asymmetric broadening to lower energy) for different diameters of Si nanowires and the Lorentzian line shape of the bulk (equation 4.43) for comparison.

In the case where the Raman spectrum is due to an assembly of nanowires, the diameter distribution should be taken into account. In this case, the Raman lineshape is given by

\[
I_{NW,D} = \int N(D)I_{NW}(\omega, D) dD ,
\]

( 4.44 )
where $N(D)$ is diameter distribution ($D = 2r_o$). The reader can refer to chapter 3 section 3.2.1 for details of the diameter distributions. Shown in Figure 4–11 is a comparison of the Raman lineshape for 8nm Si nanowires and the lineshape corresponding to an experimentally measure log-normal diameter distribution (cf Figure 3–1c). Clearly, the diameter distribution causes a small downshift in frequency and a significant broadening of the line; in this case ~ 1cm$^{-1}$ downshift in the peak position and ~30% line width broadening are calculated for the real $N(D)$. 
Figure 4–11: Comparison of the Raman line shape of 8nm diameter Si nanowires, taken diameter distribution into accounts (solid line, equation 4.44) and without diameter distribution (dashed line, equation 4.41). The peak downshift \( \sim 1 \text{ cm}^{-1} \) and the linewidth broadened \( \sim 30\% \)

4.7 Fano Interference Effect

The Raman lineshapes calculated from Richter’s model also resemble that of Fano Interference scattering. In fact, it appears to us that both confinement and interference scattering is required to explain the experimental data for Si and Ge. We therefore review Fano interference scattering. In his investigation of the many-particle interaction between continuum states and discrete levels,
Fano [40, 41] demonstrated the existence of an interference between these states. If both sets of states participate in a Raman scattering process, the interference distorts the spectral profiles of both the discrete scattering states (e.g. phonons) and the continuum scattering states (e.g. phonon, or electronic). Since then, the Fano interference effect has been observed in many areas of nuclear, atomic, molecular and solid state physics. There are numerous examples of discrete levels interfering with a continuum of states: such as a discrete phonon line coupled to a two-phonon continuum [42, 43].

In some doped semiconductors: such as Si, either $p$-type or $n$-type, electronic excitations can interact with phonons, *when the discrete optical-phonon state has the same symmetry as the interband electronic transition*. An interference between the discrete phonon state and the electronic continuum then can take place which leads to a modification of the Lorentzian lineshape, to that of the asymmetric Fano-type lineshape [40, 41]. In n-doped Si or Ge, for example, the Raman profile is asymmetrically broadened towards the lower energy, whereas in p-doped Si or Ge, the line is asymmetrically broadened towards higher energy. The profile of the first order Raman active band in $p$- and $n$-type doped Si [44-46] is a classic demonstration of this Fano effect [40, 41]. In Figure 4–12 we show a schematic illustration of the Fano interference process. In the figure, there is ground state $|g>$, an exited electronic state $|e>$ of energy $E_e$ and one phonon excited state $|p>$ of energy, $E_p = h\omega_p$. The electron-phonon interaction matrix element $<e|H_{ep}|p>$, and the transition matrix element connecting the ground state to the phonon and the electronic states are, respectively, $T_p$ and $T_e$. The Fano function describing the asymmetric line shape of the Raman active phonon modes interfering with a featureless (constant) continuum can be written as [40, 46, 47]:
Figure 4–12: Schematic illustration of the states and transitions involved in a Fano interference between an electron continuum state and a phonon discrete state. $|g\rangle$, $|p\rangle$ and $|e\rangle$ are the ground state, the phonon state and the electronic excited state, with corresponding energies $E_g$, $E_p$ and $E_e$, respectively. $T_e$ and $T_p$ are the transition matrix elements coupling the ground state to the electronic excited state and the phonon state respectively. $V$ is the electron-phonon interaction matrix element that mixes $|e\rangle$ and $|p\rangle$.

where

$$f(\varepsilon, \alpha) = \frac{(\alpha + \varepsilon)^2}{1 + \varepsilon^2}$$  \hspace{1cm} (4.45)
\[
\frac{E - E_p - V^2 R(E_p)}{\pi V^2 D(E_p)}, \quad (4.46)
\]

\[
q = \frac{VT_p / T_e + V^2 R(E_p)}{\pi V^2 D(E_p)}, \quad (4.47)
\]

and

\[
\Gamma = \pi V^2 D(E_p) \quad (4.48)
\]

Here, \(q\) is a dimensionless coupling parameter, \(E_p = \hbar \omega\) is the phonon energy of the bulk semiconductor crystal, \(T_p\) and \(T_e\) are Raman matrix element for phonon and electron scattering, respectively. \(V\) represents the electron-phonon interaction. \(R(E_p)\) represent the density of states (DOS) for continuum scattering evaluated at the phonon frequency \(\omega = E_p / \hbar\). The continuum DOS is approximated as a constant.

\[\text{Figure 4–13: The Fano lineshape from equation 4.45 for Si with } \alpha = \pm 15, \ \Gamma = 6.5 \ \text{cm}^{-1}, \ \omega_o = 521\text{cm}^{-1} \text{ (left), and } \Gamma = 6.5 \ \text{cm}^{-1}, \ \omega_o = 519\text{cm}^{-1} \text{ (right).}\]
$D(E)$ is the density of continuum states and $R(E)$ is the Hilbert transformation. i.e.,

\[
D(E_p) = \sum_e \delta(E_e - E_p)
\]

(4.49)

\[
R(E_p) = P\int \frac{D(E')}{E - E'} \, dE'
\]

(4.50)

where P is the principal value [40, 46, 47]. Plots of equation 4.45 for $q = 15$ and $q = -15$ are shown in Figure 4–13. These choices of $\alpha \pm 15$ are consistent with Fano scattering from a p- and n-Si material, respectively.

4.8 Coupled Phonon Confinement and Fano Interference Phenomenon

The previous sections in this chapter have dealt in detail with discussions of phonon confinement and Fano interference. It is worth considering that in quantum dots and nanowires both effects might occur simultaneously. In this section, we consider how the Raman spectrum would appear if these effects took place together. This is important because both the Fano interference and phonon confinement can contribute to the Raman line asymmetry. Depending on the sign of the Fano coupling parameter, the resonance either “adds” or “subtracts” asymmetry from the phonon confinement lineshape. For a typical semiconductor with $\partial \omega / \partial q < 0$ near $q = 0$, a negative Fano coupling parameter ($\alpha$) will enhance the asymmetric broadening to lower frequency whereas a positive Fano coupling parameter will diminish the phonon confinement effect. This can be inferred from Figure 4–10 and Figure 4–13. We next consider a modification to Richter’s phonon confinement model by including Fano interference.
scattering. The Lorentzian in equation 4.41 is replaced by the Fano function equation 4.45 and we have for the scattered intensity

\[ I(\omega) = \int_0^1 \exp\left[ -\gamma (q^2 r_0^2) \right] \frac{1}{1 + q^2} \, dq \]  

\[
(4.51)
\]

where \( \exp -\gamma (q^2 r_0^2) \) is the Fourier transform of the Gaussian localization function and \( \epsilon \) is given by:

\[
\epsilon = \frac{\omega - \omega_p (q)}{(\Gamma/2)}
\]

\[
(4.52)
\]

where \( \Gamma \) is the FWHM of the Lorentzian lineshape that would be obtained if \( 1/\alpha \to 0 \). In the limit of large \( \alpha \) equation 4.51 reduces to Richter’s 4.41. We have not included the diameter distribution \( N(D) \) at this point, to do this is straight-forward and requires a second, numerical integration (c.f., equation 4.44)

---

**Figure 4–14**: A comparison of the plot of the phonon confinement function (equation 4.41), the Fano function (equation 4.45) and the modified Fano function (equation 4.51) for a 10nm Si nanowire for \( \alpha = -15 \).
Shown in Figure 4–14 is a comparison of the plot of the phonon confinement function (equation 4.41), the Fano function (equation 4.45) and the modified Fano function (equation 4.51) for a 10nm Si nanowire for $\alpha = -15$. As can be seen, the linshapes depend on the strength of the Fano coupling parameter $\alpha$ that controls the “Fano” contribution and the wire diameter $d$ that controls the “confinement” contribution.

### 4.9 Effects of Photo-thermal and line broadening mechanisms on the Raman lineshape in Si, Ge

The study of line broadening and shift in the phonon modes of materials is of much interest, since it can provide detailed information. In semiconductors, it is well known that tensile and compressive stress causes the Raman band to red-shift and blue-shift, respectively. This effect is not sensitive to temperature. In disordered and low dimensional systems (nanowires and quantum dots), we have learned that the one-phonon Raman band is either asymmetrically broadened to higher or lower frequency, depending on the sign of the phonon dispersion, i.e., $d\omega/dq < 0$. Another process that leads to asymmetric broadening in the bulk is the Fano interference effect, as explained in the previous sections. In some cases, thermally induced processes are known to contribute to a downshift and a broadening of the 1\textsuperscript{st} order Raman band in Si and Ge with increasing temperature as a result of a softening of the lattice parameter. It is also known that Photo-induced processes can lead to a Fano lineshape, causing an asymmetric broadening in the Raman band. In this work, we have evidence that both thermal-
and photo-stimulated contributions to the 1st order Raman scattering of Si and Ge nanowires occur.

4.9.1 Thermally-induced Broadening in Ge and Si Phonon Modes

Experimental studies of the inelastic scattering of light by crystals have provided a great deal of information concerning the optical modes of vibration at the center of the Brillouin zone. In pure crystals, one finds typically that both the peak frequency and the linewidth vary with temperature. This temperature dependence can be attributed to the anharmonic terms in the lattice potential energy[48-50]. Cowley carried out theoretical investigations of the temperature dependence of Raman-active phonons in bulk Ge and Si using cubic anharmonic terms in the lattice potential [51]. Using neutron scattering data for the phonon dispersion of Si and Ge, Cowley[51] carried out numerical calculations using the anharmonic theory developed by Kokkedee [48], Maradudin and Fein[49] and by Cowley[50]. In this approach, Cowley was able to calculate the frequency and the linewidth of one-phonon Raman band at 10, 100, 300 and 500K. If one restricts oneself to cubic anharmonicity in second order, as was done by Cowley [51], the damping constant (Γ) which characterizes the linewidth is proportional to the absolute temperature $T$ in the high temperature limit. However, including the quartic anharmonicity to second order and/or cubic anharmonicity to the forth order, the damping constant involves terms proportional to $T^2$ in the high temperature limit [52]. Raman scattering studies on Si at room temperature were first published by Russell [53] and then by Parker [54]. The experimentally determined linewidths for the 520 cm$^{-1}$ phonon were several times smaller than the values calculated by Cowley [51]. Klemens then suggested a modification of cubic anharmonicity
theory by assuming that the lifetime of the zone-center optical phonon was limited by its decay to two longitudinal zone-edge acoustic phonons. This ansatz yielded a smaller estimate for the linewidth, in better agreement with Parker and coworker [54]. Since then, detailed studies of the temperature dependence of the first order Raman band in Si and Ge over a temperature range from 20–770K have been reported by Hart [55], Ray [56] and Cerdeira [57] and their coworkers. The experimental results for the phonon frequency shift with temperature were in good agreement with Cowley’s calculation [51] which is given by

\[ \Delta(T) = AT + B \left( 1 + 2e^{\frac{\hbar \omega_o}{kT}} \right). \]  \hspace{1cm} (4.53)

The first term of the right hand side is the contribution to the shift from lattice expansion, the constant \( B \) determines the cubic contribution to the decay process, \( \omega_o \) is the optical phonon peak frequency at \( T = 0 \). However, the temperature dependence of the observed Raman linewidth were found in serious disagreement with Cowley’s [51] calculations. Hart and coworkers [55] later successfully interpreted the temperature dependence of the linewidth of Si on the assumption that the lifetime of the zone-center optical phonon is principally limited by its decay to two degenerate longitudinal acoustic phonons with energy equal to one half of that of the optical phonon, as proposed by Klemens [58]. According to the model, the Full Width at Half Maxima (FWHM) is given by

\[ \Gamma(T) = \Gamma(0) \left[ 1 + 2 \left( e^{\frac{\hbar \omega_o}{kT}} - 1 \right)^{-1} \right], \]  \hspace{1cm} (4.54)

where \( \Gamma(0) \) is the FWHM at \( T = 0 \). This model was also successfully used to explain the temperature dependence of the linewidth in Ge within the same temperature range [56, 57]. Tsu
and Hernandez [59] also have reported measurement of the frequency shifts of both the one-phonon and two-phonon Raman bands in Si over the temperature range 20–900 °C. Their results were found in good agreement with that of Hart [55], Ray [56] and Cerdeira [57] and their coworkers. Recently, Balkanski and coworkers extended the Klemens-Hart-Aggarwal-Lax model to include a quartic anharmonic contributions (four-phonon process) to provide an even better fit to their data for the frequency and the damping constant of the first order Raman active mode in Si up to 1400 K. With these improvements the expressions for $\Delta(T)$ and $\Gamma(T)$ become more complicated [33]

$$\Delta(T) = C \left[ 1 + \frac{2}{e^x - 1} \right] + D \left[ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (4.55)$$

and

$$\Gamma(T) = A \left[ 1 + \frac{2}{e^x - 1} \right] + B \left[ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (4.56)$$

where $x = h \omega_0 / 2kT$, $y = h \omega_0 / 3kT$ and $A$, $B$, $C$ and $D$ are constants. In the high-temperature limit, the first and the second terms in the above equations vary as $T$ and $T^2$, respectively, i.e.,

$$\omega(T) = \omega_0 + CT + DT^2$$

and

$$\Gamma(T) = AT + BT^2 \quad (4.57)$$
4.9.2 Photo-stimulated asymmetric line Broadening in the Phonon modes of Ge and Si nanowires

In solids, particularly semiconductors, electronic excitations can interact with phonons leading to modification of the phonon frequency as well as the phonon lifetime. Changes in the one-phonon band frequency and linewidth were reported by Cerdeira and coworkers for n- and p-degenerately Si doped [57]. The first order Raman bands in heavily doped n- and p-type were found to develop an asymmetric line profile characteristic of a Fano interference, i.e., coherent discrete-continuum interaction between the one phonon scattering and the Raman active continuum of electronic excitations [44, 45]. For p-type Si this takes place for almost any value of the carrier concentration [45], while for n-type Si, it takes place only above a concentration [44] estimated to be $4 \times 10^{19}$ cm$^{-3}$ [60]. However, the Fano-like asymmetry might also be the result of photo-stimulated processes from deep level impurities or from the photo-production of electron-hole(e-h) pairs[61]. Both our Si and Ge nanowires were made using Fe. Fe is one of the most important deep level impurities in Si and Ge.
REFERENCES


Chapter 5

Correlation of Nanowire Diameter to Confined Phonon from Raman Scattering in Si Nanowires

5.1 Introduction

This chapter is devoted to Raman scattering experiments on ensembles of Silicon nanowires (SiNWs) deposited on indium foil substrate. In order to preclude contributions from other processes like thermal broadening, Fano interference effect, the Raman spectra were collected at very low laser flux, 8mW/µm² and on wires with good thermal contact to substrate. Three sets of Si nanowires of most probable diameter 6.5nm, 9.5nm and 23nm were studied. These wires were made by in situ oxidation PLV synthesis process and centrifugation. We observed a diameter dependent asymmetric broadening in the triple degenerate 1st order LO–TO phonon mode of SiNWs (q = 0) consistent with the Richter’s model. To the best of our knowledge, this work is the first to systematically study the asymmetry and wire diameter. The model of Richter et al., using a Gaussian localization function \( \exp\left[-\alpha(r/r_o)^2\right] \), where \( D_o = 2r_o \) is the diameter of the Si crystalline core and \( \alpha \) is a dimensionless parameter, fit our data with \( \alpha \approx 1 \pm 0.1 \). Our results indicate that the inherent diameter distribution of the nanowires also makes a contribution to the total Raman linewidth (~30%). We have used Transmission Electron Microscopy to determine the diameter distribution and to investigate the crystallinity.
In several reports in the literature [1-8], a wide diameter distribution is usually observed for SiNWs [5-8]. Previously, it has been observed that the diameter distribution plays a very important role in the lineshape of photoluminescence (PL) peak of SiNWs [8,9]. Two previous observations of a downshifted and asymmetrically broadened Raman feature near ~500 cm\(^{-1}\) in SiNWs have been reported[10,11]. So it is surprising that the diameter distribution has not being an issue in interpreting the Raman scattering from NWs. These studies fit their data using a mean diameter and not the actual diameter distribution. As is often the case in quantum confined systems, the size distribution, if not sufficiently monodisperse, broadens the resonance, or diminishes the clarity of the confinement effects. We find this is also the case when probing a real Si-nanowire sample by Raman spectroscopy. Since the Raman band downshifts due to a quantum size effect (i.e., phonon confinement), the real diameter distribution must also be incorporated in the Raman data analysis. To the best of our knowledge, we are the first to build in the measured diameter distribution of the nanowires into the Raman line shape calculation. Doing this establishes the value of the scale factor \(\alpha\) in Richter’s model [12]. For fixed \(\alpha\), a lineshape analysis of the TO mode could then yield the most probable wire diameter and the characteristic width of the diameter distribution on the chip. Apart from phonon confinement, other phenomena such as flux-induced Fano interference; thermal broadening and strain effects on the lineshapes were not considered in previous reports[10,11,13]. Discussions of these effects are postponed to the subsequent chapters.
5.2 Experimental Details

The silicon nanowires (SiNWs) in this work were prepared by pulsed laser vaporization (PLV) of a Si target containing \(~10\) atomic percent of Iron. Details are given in Chapter 2. In brief, a target of 12 mm in diameter, 8 mm thick was prepared by pressing well-mixed micron size 99.999\% pure Si and Fe powders (from Alfa-Aesar Inc.). The target was centered in a quartz tube with an inner diameter of 25 mm that passed through a one-meter long tube furnace. The target was heated to 1200\(^\circ\) C, as determined by an internal inconel-sheathed thermocouple placed just behind the target. UHP Argon with 10\% hydrogen mix gas (99.999\%) passed down the axis of the quartz tube at 100sccm, and in the same propagation direction as the incident beam from a pulsed Nd:YAG laser (10 Hz repetition rate; Spectrum Laser System, Model SL803). Both the fundamental (1064 nm) and first harmonic (532 nm) were focused on the target, respectively, at a pulse energy of 950 mJ/pulse and 320 mJ/pulse. The fundamental IR pulse was delayed by 50ns with respect to the visible harmonic pulse. The short duration, high intensity pair of laser pulses caused a vapor plume of Si and Fe to be ejected normal to the target. The gas flow reverses the direction of the Fe/Si mass flow (plume) leaving the target, and NWs deposit on the tube walls behind the target. The growth process is via the vapor-liquid-solid (VLS) mechanism as discussed in Chapter 2. The SiNWs studied here were removed from the wall of the quartz tube. High-resolution transmission electron microscopy (HRTEM) using a JEOL (JEM 2010F) microscope with a 100 kV accelerating voltage was used to observe the NW crystallinity and SiO\(_2\) coating. The TEM grids was prepared by suspending a small amount of NW material in ethanol, and using an ultrasonic horn (Misonix Inc., #XL 2010) operated at 100 W was used to dispersed it in the ethanol.
Raman spectra were collected at room temperature in the backscattering configuration using a JY Horiba T64000 spectrometer equipped with a 640mm subtractive-double pre-monochromator followed by a 640mm spectrograph with cooled CCD detection. An Olympus BX40 confocal microscope was used to illuminate the sample and collect the scattered light. It was set to operate at a \(~ 1\mu\text{m}\) diameter focal spot size at the plane of the sample. An Argon ion laser was used to excite the spectra. The flux at the sample was \(~ 8\) \(\mu\text{W/}\mu\text{m}^2\) as measured using a miniature, hand held radiometer. The spectra were collected in air under ambient conditions using 514.5 nm laser line. Both H and V polarized light were accepted in the scattered radiation.

5.3 Results and Discussion

In Figure 5–1 we show, the HRTEM/TEM images of our SiNWs used. The diameter distribution of the three sets of Si nanowires of most probable diameters 6.5nm, 9.5nm and 23nm are shown in Figure 5–2 as histogram plots. Image analysis software (NIH image software;http://rsb.info.nih.gov/nih-images) was used on the HRTEM images to measure the lateral dimension of the crystalline core of each nanowire perpendicular to the axis of the nanowire. Also shown in Figure 5–2 are the fits of log-normal distribution function to our data

\[
F(r) = \frac{N}{\sqrt{2\pi}\sigma}\exp\left\{-\frac{\left(\frac{\log_{10} D - \log_{10} D_o}{2(\log_{10} \sigma)}\right)^2}{2}\right\},
\]

where \(N\) is the total number of counts, \(n\) is the number of counts of particular diameter, \(D_o\) is the most probable diameter and \(\sigma\) is the distribution width parameter (see Chapter 3 for more details). Shown in the inset to Figure 5–1 is TEM the image of SiNW with a metal particle
present at the tip, indicative of the VLS growth mechanism (see Chapter 2). The HRTEM image indicates that the central core of the nanowires is crystalline Si, as demonstrated by the parallel lattice fringes. An amorphous coating is seen wrapped around the crystalline core. This coating can induce compressive strain, as we shall see. The thickness of the SiO$_2$ on these NWs is $\sim$ 3 to 4 monolayers.

*Figure 5–1*: representation of TEM/HRTEM images of Si nanowires used in this study. The oxide layer wrapping the crystalline core is $\sim$3 to 4 monolayer. The inset in the TEM is the growth seed indicative of VLS growth mechanism.
Figure 5–2: The diameter distribution of the three sets of Si nanowires studied here. A log-normal fit (solid line) to the distribution (curved) is also shown. From top to bottom, the most probable diameters and standard deviation are (d = 6.5nm ± 0.3nm, $\sigma = 1.38 \pm 0.13$), (d = 9.5nm ± 0.3nm, $\sigma = 1.99 \pm 0.15$) and (d = 23nm ± 0.7nm, $\sigma = 2.99 \pm 0.50$), respectively.
In Figure 5–3a, we show the room temperature Raman spectra of the three sets of SiNWs supported on an indium foil substrate, and that of the bulk for comparison. The solid lines are fit to the data. The Raman spectra were collected from a low wire density region such as shown in Figure 5–3b. The reason for this is: 1) to provide good thermal anchorage of the wires to the substrate, 2) to use a substrate that doesn’t exhibit a Raman spectrum. The SiNWs were deposited by putting a drop of Si NW:ethanol solution on the substrate and allowing the ethanol to evaporate at room conditions. The spectra were taken with our Raman microprobe using 514.5 nm radiation line at a low laser flux of 8 μW/μm², as measured at the sample using a hand-held radiometer. The first order spectrum of the bulk Si at 520.0 cm⁻¹ is in good agreement with the literature [11]. The lineshape of the bulk phonon is well fit by a symmetric Voigt function which is a convolution of approximately Gaussian spectrometer function and a Lorentzian Raman line. The full width at half maximum (FWHM) of the bulk Si Raman line is ~ 4.5 cm⁻¹. The natural line width for the triply degenerate LO−TO phonon of bulk Si is reported to be 4 cm⁻¹ at 300K [12,14]: so, our instrument adds ~1.5 cm⁻¹ to the natural line width. It should be noted that the resultant band width for a Lorentzian line convoluted with a Gaussian instrument function do not simply add but are related by equation 3.17(Chapter 3, section 3.6.1). When compared to the true convolution the error from such an addition is ~ 22 %. However, it decreases rapidly with increasing convoluted linewidth and thus become insignificant at larger linewidth. We can see that the nanowire Raman lineshape is asymmetrically broadened to lower frequency in the case of mean diameters 9.5nm and 6.5nm, whereas there is no observable asymmetry in that of the 23nm nanowires. The band maximum has downshifted to 519.0 cm⁻¹ (d = 9.5nm) and 517.8 cm⁻¹
(d = 6.5nm) relative to the bulk symmetric band at 520.0 cm$^{-1}$. The 23nm nanowires exhibit a band at 520.0 cm$^{-1}$ in good agreement with the bulk.

Figure 5–3: a) The Raman spectra of different Si nanowire diameter collected at 8mW/µm$^2$ from a low wire density region on Indium substrate. The solid curves are the fit of equation 5.9. b) SEM image representation of the low wire density region.

We now analyze the lineshape of the SiNWs Raman band for the three sets of wires along the lines first proposed by Richter et al [12], and extended by Campbell et al [15]. The general idea behind the downshifted and asymmetrically broadened line is as follows. The “confined” transverse optic phonon in the 1D wire has a wave function that can be written as the product of the infinite crystal (or bulk) phonon wavefunction, $\Psi_{\text{bulk}}$ and a “localization” function $W(r,r_o)$ [12]

$$\Psi_{\text{NW}} = W(r,r_o)\Psi_{\text{bulk}}(\omega_{\text{TO}},0) \quad (5.2)$$
where

\[ W(r, r_o) = \frac{1}{2\pi} \exp\left[ -\alpha (r/r_o)^2 \right] \]  \hfill (5.3)

localizes the zone center, Raman-active bulk phonon \( \Psi(\omega_{\text{TO}}, q = 0) \) in a cylinder aligned along the nanowire axis (z-axis) [12,15]. The Gaussian form of the localization function \( W(r, r_o) \) amounts to “soft” confinement, i.e., the phonon wave function is non zero at the boundary of the nanowire. Next, we expand \( \Psi_{\text{NW}} \) in bulk phonon basis functions centered at \( q = 0 \) [12],

\[ \Psi_{\text{NW}} = \int C(\bar{q}, 0) u(0, \bar{r}) e^{i\bar{q} \cdot \bar{r}} d^3q \]  \hfill (5.4)

where \( u(0, \bar{r}) \) is identified with the phonon wave function \( \Psi = u(0, \bar{r}) e^{i\bar{q} \cdot \bar{r}} \) for the infinite crystal, but for \( q = 0 \). \( C(\bar{q}) \) is the Fourier transform of the localization function \( W(r, r_o) \). As expected, \( C(\bar{q}) \) is also a Gaussian, i.e.,

\[ C(\bar{q}, 0) \cong \exp\left[ -\beta (q_{\perp} r_o)^2 \right] \]  \hfill (5.5)

where \( q_{\perp} \) is the length of the radial wavevector perpendicular to the NW axis. \( C(q_{\perp}) \) depends on only \( q_{\perp} \), since \( W(r) \) does not depend on \( z \) (longitudinal or axial direction) and \( \beta \) is a fitting parameter that defines the confinement. For \( \beta = 1 \), it can be shown that \( q_o = 1/D_o \) (\( D_o = 2r \)). That is, the stronger the real space localization (\( r_o \rightarrow 0 \)), the further one must depart into the Brillouin zone to describe the confined TO phonon wave function in the NW. The Raman intensity for the "confined" TO phonon in a nanowire of radius \( r_o \) is then written as[12]

\[ I_{\text{NW}}(\omega, r_o) = \int \left| C(q_{\perp}, 0) \right|^2 L(\omega) 2\pi dq_{\perp} \]  \hfill (5.6)

where \( L(\omega) \) is the Lorentzian function given by
Thus in the limit of large wires, equation 5.6 reduces to a Lorentzian. We note that equation 5.6 is just the sum of the contributions from the Raman-active bulk phonons \((q_\perp \neq 0, q_\parallel = 0)\) in the TO branch with frequency \(\omega(q_\perp)\), but weighted by \(|C(q_\perp)|^2\), and where the bulk phonon wavefunction has been approximated by \(\Psi(q_\perp) = u(0,r)e^{i\mathbf{q}\cdot \mathbf{r}}\). It should be noted that the full width at half maximum (FWHM), or \(\Gamma\) in equation 5.7 is set to the value of the instrumental broadened Si line (bulk), since the calculation will be compared with experimental data. The instrument resolution was \(\sim 1 \text{ cm}^{-1}\) and \(\Gamma\) was observed to be \(4.5 \text{ cm}^{-1}\). To do the integral (5.6), we must know the phonon dispersion relation \(\omega(q_\perp)\). We approximate the dispersion of the TO branch for \(q_\perp\) to the SiNW axis by using an isotropic dispersion

\[
\omega_\perp(q_\perp) = \left[ A + B \cos \frac{mq_\perp}{2} \right]^{1/2}
\]  
(5.8)

where \(A = 1.714 \times 10^5 \text{ cm}^{-2}\) and \(B = 1.00 \times 10^5 \text{ cm}^{-2}\) fit the neutron scattering data for the TO branch [16, 17]. Finally, we must take into account the nanowire diameter distribution \(F(r)\) for our sample. The computed Raman lineshape for a nanowire distribution then takes the form

\[
I_{NW}(\omega) = \int_0^r F(r) I_{NW}(\omega, r) \, dr
\]  
(5.9)

where \(F(r)\) is the diameter distribution that we approximate by a log-normal distribution (Figure 5–2), and \(I_{NW}(\omega, r)\) is the calculated spectrum for a single NW of radius \(r\) (Eq.5.6). Equation (5.9) therefore amounts to evaluating a double integral, one for the diameter distribution, and the other over q-space (Equation 5.6). The constant \(\alpha\) that defines the range of \(W(r, r_0)\) (Equation

\[
L(\omega) = \frac{A}{[\omega - \omega_\perp(q_\perp)]^2 + (\Gamma/2)^2}
\]  
(5.7)
5.2) must be chosen to best fit the data. A commercially available software package, Mathematica version 5.1 (Wolfram Research Inc.) was used to evaluate the integrals (5.6) and (5.9). The fit of equation 5.9 to the Raman spectra of the different sets of wires are shown in Figure 3a as solid lines.

Let us consider the Raman spectrum of the 6.5nm nanowire to further elaborate on the fitting process. In Figure 5–4 we compute the confined TO phonon lineshape (solid lines) for several values of $\alpha$ using Equation (5.9). In Figure 5–4, we use the phonon linewidth (FWHM) of 4 cm$^{-1}$ the intrinsic bulk value 300K. As discussed above, we set $\Gamma = 4$ cm$^{-1} + 1.5$cm$^{-1}$ in equation (5.6) adding the FWHM of the instrument resolution ($\sim$ 1.5cm$^{-1}$) to the Lorentzian phonon linewidth (4 cm$^{-1}$). It should be noted that there are no adjustable parameters (other than $\alpha$) in the calculated lineshape, i.e., the distribution $F(r)$ is measured, and $\phi(q_{\perp})$ is determined by neutron scattering data [16]. As can be seen in the Figure 5–4, we find $\beta \cong 1 \pm 0.1$ gives very good agreement between the phonon confinement, and the Raman data. In two previous reports concerning phonon confinement in SiNW[10,11], it was found that the calculated linewidth is smaller than the experimentally observed line widths. In Figure 5–5, we show the effect of neglecting the nanowire diameter distribution. Shown in the figure are our data (open squares) and two computed lineshapes: (1) the Raman band lineshape for a single nanowire with the most probable diameter in the distribution (dashed line), and (2) the lineshape taking into account the diameter distribution $F(r)$ (solid line). The same TO dispersion $\phi(q_{\perp})$ and $\beta \cong 1.0 \pm 0.1$ were used to compute both lineshapes. As can be seen in Figure 5–5, the diameter distribution accounts for $\sim$ 30% of the line width. This is the second important result from our study, i.e., the sample diameter distribution can make an important contribution to the linewidth.
Finally, let us consider the third important results of this work, i.e., the evolution of the diameter with linewidth and peak position. In Figure 5–6 a and Figure 5–6 b, we show respectively the variation of the peak position and linewidth with diameter. Both graphs suggest that the linewidth and the peak position evolve exponentially with the diameter. The fit in both case is an exponential functions of the form:

*Figure 5–4:* Fit to equation 5.9 to the 6.5nm Raman data for different values $\beta = 0.75, 1$ and 1.25. The data is best fitted when $\beta = 1$. 
Figure 5–5: comparison of equation 5.6 shown as dashed curve (single wire phonon confinement) and eq.5.9 (solid curve) including diameter distribution. The distribution contributes ~30% to the linewidth. Also shown is the Raman data of the 6nm Si nanowires.

\[
\omega(d) = \omega_o + A \exp\left[\frac{d}{\tau_o}\right] \tag{5.10}
\]

for the frequency dependence, with \(\omega_o = 520.0 \text{cm}^{-1}\), \(A = -22.4 \text{cm}^{-1}\) and \(\tau_o^{-1} = 0.371 \text{nm}^{-1}\), and

\[
\Gamma(d) = \Gamma_o + A' \exp\left[\frac{d}{\tau_r}\right] \tag{5.11}
\]
with $\Gamma_o = 6.7 \text{ cm}^{-1}$, $A' = 62.5 \text{ cm}^{-1}$ and $\tau_r^{-1} = 0.439 \text{nm}^{-1}$. The larger value of $\Gamma_o$, $6.7 \text{ cm}^{-1}$ instead of $5.5 \text{ cm}^{-1}$, also support the fact that the diameter distribution contribute to the linewidth $\sim 1.2 \text{ cm}^{-1}$ which is $\sim 30%$ of $4 \text{ cm}^{-1}$ of the bulk at 300K as estimated previously.

---

Figure 5–6: evolution of a) frequency and b) linewidth with diameter for Si Nanowires. Both graphs depict an exponential dependence.

5.4 Conclusions

We have found that a simple phenomenological confined phonon model of Richter et al. [12] and Campbell et al. [15] describes well the downshifted and asymmetrically broadened experimental lineshape for 6.5nm, 10nm and 23nm core diameter Si nanowires. If the diameter distribution of the nanowires is taken explicitly into account, we find that a simple Gaussian phonon localization function ($\beta = 1$) fits the data very well with no other adjustable parameters. Eventually, for very small NW diameters, this model must fail to give an accurate description of the confined phonons, and specific calculations of the Raman spectra, including the phonon dispersion and Raman matrix element, must be carried out [18]. It should be noted that Equation
(5.9) could be used to fit the experimental TO lineshape (for $\beta = 1$), using the parameters of the log-normal NW diameter distribution as fitting parameters. This amount to a three-parameter fit, the third parameter is simply a scale factor. Also the diameter distribution has significant effect (~30%) on the phonon linewidth.

Finally, this is the first report of attempting to correlate the Raman lineshape parameters and the diameter of the nanowires. We also found out that, the Raman band peak position and linewidth evolve exponentially with diameter. Further work at low temperatures and studies on isolated individual Si nanowires is required to further support these results.
REFERENCES


6.1 Introduction

In this chapter, we investigate laser power related issues on first order Raman band in Si nanowires. The Raman experiments were conducted under two conditions: high wire density and low wire density corresponding to poor thermal anchorage and good thermal anchorage on substrate. Our observations depend on the wire density, the wire diameter, the thermal anchorage of the wires on the substrate and the thermal properties of the substrate. Our observations are explained in terms of lineshape stemming from both phonon confinement and Fano interference scattering. In its simplest form Richter’s[1] result for the Raman lineshape of a phonon confinement process is given by

\[ I(\omega, q) = \int_{0}^{1} |C(0, q)|^2 L(\omega) dq^3 \]  

(6.1)

where \( q \) is the phonon wave vector, \( |C(0, q)|^2 \) is the Fourier transform of the localization function and \( L(\omega) \) is a Lorentzian describing the Raman contributions from a single phonon. Thus one calculates via (6.1) for a system like Si nanowires the results such as shown in Figure 6–1a as discussed previously. In Figure 6–1b, we show that for Si nanowires (mean diameter = 6.5nm) it is also possible to induce Raman band asymmetry just by increasing the laser flux. The data are
similar to that published recently by our group [2], but for a different batch of nanowires that are more systematically studied in this work. In Figure 6–1b, it is clear that one can induce an asymmetry via laser flux that is similar to that anticipated Richter’s model [1]. So, it is imperative to know which reason is behind the asymmetry we observe in the 1st order band of Si nanowires. It is also clear that Richter’s model should be applicable to data collected at sufficiently low laser power!

Figure 6–1: a) diameter dependent asymmetry for Si nanowires calculated using the phonon confinement function equation 6.1, and b) flux dependent of the Raman lineshape of the first order band of Si nanowires

In this chapter, we will also demonstrate that laser-induced heating can also be observed. In fact, all these effects can occur at once. We will show that Fano scattering attributed either to a photo-stimulated and/or thermally driven electronic continuum can occur. Thermal broadening, as a result of anhamonic interaction is also possible.
6.2 Experimental Details

The details of the experimental procedure are as discussed in section 5.2 of Chapter 5. However, here we focused on two sets of SiNWs; small wires (d = 6.5nm) that exhibit phonon confinement effect and large wires (d = 23nm) that does not. Also, in the Raman scattering experiment, we considered two sets of wire densities: low wire density (good thermal anchorage to the In substrate) and high wire density (poor thermal anchorage to the In substrate) schematically shown in Figure 6–2.

Figure 6–2: the two representation of the wire densities for the Raman scattering studies: a) low wire density and b) high wire density. Nanowires were deposited on Indium foil substrate.

In Figure 6–3 we show the HRTEM/TEM images of the two sets of wires of most probable diameter 6.5nm and 23nm. The corresponding diameter distribution is shown as a histogram in Figure 6–4. The solid line is a least square fit of a log-normal function to the distribution.
Figure 6–3: HRTEM (top) and TEM (bottom) images of the two sets of Si nanowires: top) small wires of 6.5nm most probable diameter, and bottom) large wires of 23nm most probable diameter.
Figure 6–4: The diameter distribution of: top) small wires of 6.5nm diameter and, bottom) large wires of 23 most probable diameter. The solid line is the log-normal plot of the diameter distribution.
6.3 Results and Discussion

Breit-Wigner-Fano (BWF) interference effect involving the interaction of the discrete phonon states and the electronic continuum have long been studied extensively in first order Raman lineshape of doped bulk Si[3-8]. The sign of the asymmetry parameter \((Q)\) depends on the type of dopant: i.e. n-type or p-type. The degree of asymmetry depends on the doping concentration. p-doping causes asymmetric broadening to higher energies[7, 8] whereas the n-doping does the reverse[3, 6]. In the BWF process, the electrons have to redistribute themselves in time much shorter than the period of the perturbation; in this case the long wavelength optical phonons. In Si, the optical phonon frequency \(\omega_o \sim 10^{13} \text{s}^{-1}\). The effect of free electrons on \(\omega_o\) depends on the ability of the carriers to redistribute themselves in the time shorter than the period of \(\omega_o\). If \(\tau_e\) is a typical redistribution time, then the Fano interference effect can be observed only if

\[\omega_o \tau_e \leq 1 \quad (6.2)\]

For a n-doped bulk Si [3, 5], it has been noted that continuum Raman allowed scattering must arise from the electronic transitions between the \(\Delta_1\) and \(\Delta_2\) conduction bands which are degenerate at \(X_1\) along the X direction in the Brillouin zone, as shown in Figure 6–5. However, in small wires (\(d \leq 10\text{nm}\)) the optical transitions might be modified by quantum confinement as has been reported in photoluminescence from 15nm diameter SiNWs [9,10]. In our Si nanowires, Fe was used as the metal agent in the growth process which is also a deep level donor impurity in bulk Si at 0.39 eV. Such impurity state might contribute to the Fano interference process.
In Raman scattering from nanostructures where phonon confinement and Fano interference effects might both contribute to the Raman line we propose a modification to Richter’s model given by:

\[ I(\varepsilon, q_{\perp}) = \int_{q_{\perp}} C(0, q) S(\varepsilon) 2\pi q_{\perp} dq \]  

(6.3)

**Figure 6–5:** Conduction bands of bulk Si near the \( X_1 \) point, where \( \Delta_1 \) and \( \Delta_2' \) bands are degenerate. \( \hbar\omega \) is the energy of a Raman-active transition between bottom of the conduction band and the edge of the Brillouin zone. \( \hbar\omega_{\text{min}} \) and \( \hbar\omega_{\text{max}} \) are the minimum and maximum transition energies between \( \Delta_1 \) and \( \Delta_2' \) bands for the Fermi level of \( E_F \). \( E_F' \) denotes the Fermi level when it has risen above the \( X_1 \) point. b) Transverse slice of the bands at energy \( \hbar\omega < \hbar\omega_{\text{min}} \) when the Fermi level has risen above the \( X_1 \) point to \( E_F' \). The shaded area denotes the region where there exists filled initial and empty final states, permitting transitions to take place [5].
where $S(\varepsilon)$ is the BWF function expressed by

$$S(\varepsilon) = S_0 \frac{(Q + \varepsilon)^2}{1 + \varepsilon^2} \quad (6.4)$$

with $Q$ defined as the Fano coupling parameter and $\varepsilon = (\omega - \omega_c)/\Gamma$. In the limit as $Q^{-1} \rightarrow 0$ (i.e., $Q \rightarrow \infty$) in equation 6.4, equation 6.3 reduces to the phonon confinement case as in equation 6.1. In Si, the lineshape derived from Richter’s model and that from Fano Interference scattering have similar shape even though the Physics behind each of these processes is entirely different (see chapter 4).

In Figure 6–6 we compare lineshape by overlapping a least square fit of a Fano function, equation 6.4 (dashed lines) to the phonon confinement function for a 1D system, equation 6.1 (solid line). We do this for 4 different diameter Si nanowires ($d = 3$nm, 5nm, 10nm and 20nm). It is obvious from the figure, that for $d > 5$nm, the two functions agree rather well. This can be understood, since in the limiting cases ($d \rightarrow \infty$, $Q \rightarrow 0$) each function reduces to a Lorentzian. We see that the mismatch in the two functions increases with decreasing nanowire diameter.

To distinguish the laser flux dependence contributions to the Raman lineshape of our SiNWs, we have considered two sets of wires; small wires of most probable diameter 6.5nm and large wires of most probable diameter 23nm. From these two sets we have prepared substrates with low wire density and high wire density. The high wire density substrates have many layers of wires on top of each other. Many wires are therefore in poor thermal contact with the substrate. The low density substrates have most of the nanowires in direct thermal contact with the substrate (i.e., they lie directly on the substrate. In Figure 6–7 and Figure 6–8, we show the
flux dependent Raman lineshape of Si NWs (d = 6.5 nm, 23nm) collected from low wire density and high wire density region respectively.

Figure 6–6: Comparison of the Breit-Wigner-Fano function lineshape to the phonon confinement function lineshape. The least square fit of the BWF function (dotted lines) to calculated first order Raman lineshape of confined phonons in Si nanowire for a) d = 20nm, b) d = 10nm, c) d = 5nm and d) d = 3nm. The lineshapes from the two functions are very similar for d > 5nm.
Low Wire Density

Figure 6–7: Flux dependence of the Raman lineshape of the first order Raman-allowed band of Si nanowires of different diameters, a) d = 6.5nm and b) d = 23nm. The Raman scattering experiment was conducted on low wire density region on Indium foil substrate. It is interesting to note in a) and b) that the peak position remains the same with increasing flux whereas an asymmetry develops with increasing flux. The Raman band of the bulk (open circle) is shown for comparison.

In Figure 6–7 (low wire density substrates) Raman spectra are shown as function of laser flux. All asymmetric broadening with increasing flux, but fixed peak position can be observed. Also for the lowest flux (8µW/µm²), a Lorentzian is observed for the large diameter wires (no confinement), Figure 6–7a, and in Figure 6–7b a noticeable asymmetry is evident for the ~6.5nm diameter wire. The Raman band for bulk Si (open circles) is shown for comparison in both Figures.
However, for the high wire density samples, (Figure 6–8) we observe a significant downshift and asymmetric broadening of the band with increasing flux.

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**High Wire Density**

![Graph showing Raman lineshape for Si nanowires of different diameters with high wire density.](image)

*Figure 6–8:* Flux dependence of the Raman lineshape of the first order Raman-allowed band of Si nanowires of different diameters, a) $d = 6.5\text{nm}$ and b) $d = 23\text{nm}$, but with high wire density. See Figure 6–7 for comparison with low wire density results. It is interesting to note in a) and b) there is a downshift with increasing flux and the asymmetry develops with increasing flux as well. The Raman band of the bulk (open circle) is shown for comparison in both Figures.

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In order to decipher the physical phenomena contributing to such asymmetric behaviors in the 1st order Raman profile of Si nanowires, we employ a non-prejudicial asymmetric parameter analysis technique [11], i.e., we analyze the line asymmetry without using either the phonon confinement or Fano functions. An asymmetry parameter ($A$) is defined by the 10% of
the maximum as the ratio of the half width at lower frequency ($\Delta \omega_l$) to half width at high frequency ($\Delta \omega_h$),

$$A = \frac{\Delta \omega_l}{\Delta \omega_h} = \frac{\omega_+ - \omega_o}{\omega_+ - \omega_-} \quad (6.5)$$

where the meaning of the $\omega_-$, $\omega_+$ are and $\omega_o$ are indicated on Figure 6–9.

---

*Figure 6–9*: A general line asymmetry parameter is defined as $A = \frac{\omega_o - \omega_-}{\omega_+ - \omega_o}$, where $\omega_-$ and $\omega_+$ are coordinates at 10% of the peak intensity.

---

In *Figure 6–10* we show the measured asymmetric parameter ($A_{\text{exp}}$) vs. laser flux for a) low wire density, small wires ($d=6.5\text{nm}$), b) low wire density, large wires ($d = 23\text{nm}$), c) high wire density, small wires ($d = 6.5\text{nm}$) and high wire density, large wires ($d = 23\text{nm}$). Note that the
behavior of the asymmetric parameter with flux is significantly different for d = 6.5nm sample at low wire density (Figure 6–10a) when compared to the others. The details of Figure 6–10 will be discussed later.

Figure 6–10: The variation of asymmetry parameter with flux for a) the Raman lineshape shown in Figure 6–7a (low wire density, small wires), b) the Raman lineshape shown in figure 6–7b (low wire density, large wires), c) the Raman lineshape shown in figure 6–8a (high wire density, small wires) and, d) the Raman lineshape shown in figure 6–8b (high wire density, large wires).
In *Figure 6–11* we show the correlation of the asymmetry parameter $A_{\text{exp}}$ with the Raman band peak frequency. Data from Figures 6–7 and 6–8 were correlated. In *Figure 6–11a*, low wire density, small wires ($d = 6.5\text{nm}$), the asymmetry decreases, reaches a minimum and increases without a change in the peak position. For large diameter wires (*Figure 6–11b*) are for low wire density, the peak position is constant while the asymmetry parameter increases.

![Graph showing variation of asymmetric parameter with peak frequency](image)

*Figure 6–11*: the variation of the asymmetric parameter with peak frequency for the corresponding graph shown in figures 6-7 and 6-8. Note that the frequency axis is reversed.

From Figures 6–10 and 6–11, it is clear that there is a rich behavior to be seen in the 1st order Raman scattering of nanowires, depending on the wire diameter and the thermal anchorage. The effect we see may or may not be intrinsic.

Considering all the results for the $d = 23\text{ nm}$ wires at low density, we can conclude that there is no phonon confinement effect and that there is negligible sample heating to the highest laser flux (i.e., no shift in peak position). The $d = 23\text{ nm}$ low wire density results indicate we have formed a good thermal sink. In wires where there is no phonon confinement and the thermal
effects are weak, the only phenomenon that can contribute to the Raman line asymmetry should be the Fano interference effect, and the process appears to be photo-stimulated. In this case the Raman lineshapes should be described by the BWF function given by equation 6.4.

Now let us consider the Raman spectra for the d = 6.5 nm wire at low density. The asymmetry parameter A decreases, reaches a minimum and then increases with increasing flux. However, there is no obvious change in the peak position with flux. To better understand such behavior, let us consider our modified phonon confinement function

\[ I(\omega) = \int_0^1 |C(0,q_\perp)|^2 S(\varepsilon) 2\pi q_\perp dq_\perp \]

(6.6)

where \( S(\varepsilon) \) is the BWF function,

\[ S(\varepsilon) = S_o \frac{[Q(\Phi) + \varepsilon]^2}{1 + \varepsilon^2} \]

(6.7)

However, now we consider the coupling parameter \( Q \) and linewidth parameter \( \Gamma \) to be simple linear functions of laser flux, \( \Phi \). Using \( \Gamma(\Phi) = \Gamma_o + a\Phi \) and \( Q(\Phi) = Q_o + b\Phi \), we generated Raman lineshapes for different fluxes and calculated the asymmetry parameter as given in equation 6.5. In Figure 6–12a and Figure 6–12b, we show the calculated asymmetry parameter (A\text{calc}) as a function of peak position and flux, respectively. The behaviors mimic the experimental results shown in figure 6–10a and Figure 6-11b for low wire density (d = 6.5nm), suggesting that both phonon confinement and Photo-stimulated Fano interference scattering play a role in the observed lineshapes. It is apparent that the rise in the asymmetry with increasing flux is mostly due to the photo stimulated Fano interference process, however, the decrease in asymmetry parameter with flux still needs to be explained.
Figure 6–12: Variation of calculated asymmetry parameter (from lineshape generated with equation 6.6 using $\Gamma = \Gamma_o + a\Phi$ and $Q(\Phi) = Q_o + b\Phi$). The calculated behavior mimics the experimental observation, confirming that both phonon confinement and Fano interference effects contribute to the observed lineshape.

To explain the initial behavior of the decrease in asymmetry with increasing flux in Figure 6–10a, let us look at the effect of temperature on the lineshape of the phonon confinement in a simplest way. The Lorentzian $L(\omega)$ in equation 6.1, is given by

$$L(\omega) = \left[\left(\omega - \omega_o(q, T)\right)^2 + \left(\Gamma(T)/2\right)^2\right]^{-1} \quad (6.8)$$

For convenience, $\omega_o$ and $\Gamma$ are assumed to be linear in $T$, which is consistent in the bulk case within the chosen temperature range[12]. Shown in Figure 6–13a and Figure 6–13b are, respectively, the theoretically calculated phonon lineshape, and the variation of the calculated
asymmetry parameter as a function of frequency. As can be seen in *Figure 6–13b*, the calculated asymmetry parameter \(A_{\text{calc}}\) decreases with decreasing frequency (increasing temperature) suggesting that the thermal broadening due to increase temperature reduces the asymmetry from the phonon confinement function due to \(\omega(q_{\perp})\). Thus the observed behavior in the Raman band of Si nanowires in *Figure 6–10a* can be understood as due to laser heating.

\[\begin{align*}
\text{Int. (arb. units)} & \quad 540 \quad 520 \quad 500 \quad 480 \quad 460 \\
\text{Frequency (cm}^{-1}) & \quad 300 \quad 400 \quad 500 \quad 600 \quad 700 \quad 800 \\
800 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
700 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
600 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
500 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
400 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
300 \text{ K} & \quad \includegraphics[width=0.3\textwidth]{figure6-13a}
\end{align*}\]

*Figure 6–13*: The calculated phonon confinement lineshape using \(\Gamma = \Gamma_{o} + c\Phi\). b) the variation of calculated asymmetry parameter for the Raman lineshape shown in a.

In *figure 6–7a* there is no observable change in the peak position with increasing flux indicating that the sample temperature did not increase enough to cause a change in peak position. However, the heating was enough to cause a change in the asymmetry. Even in the case of bulk
Si, only 1 cm$^{-1}$ change in peak position was observed within the temperature range of 300K to 400K (100$^\circ$C increase in temperature) [12]. Thus, we attribute the observed decrease in asymmetry parameter with flux in the initial part of Figure 6–10a to predominantly a thermal effect on the phonon confinement lineshape. The behavior in Figure 6–10a for 6.5nm Si nanowires is thus due to three processes: phonon confinement, temperature effect on phonon confinement and photo-stimulated Fano interference effect. In Figure 6–10a, the sample warms up with increasing flux, leading to the decrease in asymmetry parameter due to the temperature effect on the phonon lifetime $\Gamma^{-1}$. At low laser flux, the photo-stimulated contribution is not strong enough to cause any observable change. At about 0.4 mW/µm$^2$, the photo-stimulated process becomes strong enough leading to an up turn in the asymmetry parameter with increasing flux.

Now let us consider the other plots in Figures 6–10 and 6–11. We attribute the observed behavior in Figure 6–10b and Figure 6–11a (solid circles) as due to only photo-stimulated process because of large wires, implying, no phonon confinement process and/or no thermal contribution. In samples with a high wire density of small nanowires (6.5nm), the observed Raman lineshape and the behavior in Figure 6–10c and Figure 6–11a (open circles) are due to phonon confinement effects, photo-stimulated Fano interference effects and thermal broadening from sample heating. The behavior of the asymmetry parameter with flux and frequency for high wire density, large Si nanowires (23nm) is attributed to a photo-thermally driven Fano interference effect.
6.4 Conclusions

In conclusion, the observed lineshape of the Raman band of our Si nanowires stem from three phenomena 1) phonon confinement effect, i.e., the break down of the Raman selection rule that leads to a downshift and an asymmetric broadening of the first order Raman band, 2) Flux (thermal) induced asymmetry and 3) photo-stimulated asymmetry. The last two processes are attributed to Fano interference scattering between the discrete phonon states and the electronic continuum. These processes can be distinguished as follows:

Lowest laser power possible maximizes the contribution from phonon confinement. The theory of Richter et al. [1] makes a clear prediction regarding the dependence on diameter. This is tested at low powers and the lineshapes for a series of samples with significantly different mean diameter support their theory.

To distinguish between thermal and photo stimulated Fano scattering, we need to establish different thermal environments for the samples. To accentuate thermal effects, we deposit large amounts of wires on the substrate with poor thermal anchoring. The wires have difficulty dumping the heat promoted by the laser heating and the shifting and broadening of the Raman 520 cm\(^{-1}\) band is observed.

On the other hand, if the wires are deposited in low density on the substrate, the thermal anchoring is considerably improved and the effects of increased laser flux are observed to only asymmetrically broaden the line and the apparent shift in the peak position is very small.


Chapter 7

Oxidation as a means of controlled reduction of Si Nanowire Diameter

7.1 Introduction

This chapter focuses on a simple but effective technique, oxidation as a means of reducing the nanowire diameter into a range that exhibit strong quantum size effects. We follow two approaches in the dry oxidation process: \textit{ex situ} oxidation i.e., dry oxidation after the sample has been expose to the atmosphere and \textit{in situ} oxidation i.e., dry oxidation performed before the sample temperature is lowered and taken out of the growth chamber. We discuss the ramifications of these two approaches on phonon quantum confinement. To study the effect of the oxide layer on the first order Raman band in SiNWs, we also used wet etching in HF to remove the oxide layer introduced by the dry oxidation process. Wet and dry oxidation have both been widely used in the production of Si devices and have been studied extensively[1-6].

Wet and dry oxidation processes differ from one another in several points: (1) wet oxidation is more rapid [3], (2) there is less initial oxidation enhancement for wet oxidation processes [3,6] and (3) wet oxidation rate has a linear pressure dependence [5], but a sub-linear pressure dependence for dry oxidation is observed [6].

Si has dominated the semiconductor industry ever since it became the preferred material for device fabrication. As the device dimensions in VLS technology continue to be reduced, the thermal oxidation of the Si nanostructures is becoming very important. Also, the oxide layer
formed due to the oxidation process plays an important role in the electrical isolation of the Si underlayer. Oxide coated Si nanowires with small diameters \( d < 5 \) nm can provide opportunities for new Si with and novel transport and optical properties. The diameter of the nanowires can be controlled to determine the physical properties of the nanowires on the device built from these wires. There have been several reports in recent years on potential applications of Si nanowires as field effect devices [7-10] and light emitting devices [11]. Oxidative control of the nanowire diameter and device characteristics would be very desireable.

In chapter 5 we demonstrated phonon confinement effects in Si nanowires of diameters ranging from 5nm to 30nm. However, these wires are coated with an oxide and the phonons in the Si crystalline core “leaks” into the oxide, i.e., soft confinement. Thus in this chapter, examine the role of the oxide coating on the Raman scattering of the Si nanowires.

Early work on dry oxidation of 2 dimensional Si nanostructures indicated that oxide grow in the corners of the Si trenches was greatly reduced [12]. This was further studied experimentally and theoretically by Kao et al. [13] for patterned Si cylinders with diameter larger than 1\( \mu \). Liu and coworkers [14, 15] studied large Si nanowires with \( 40\text{nm}<d<300\text{nm} \) and they also studied Si columns with dimensions \( \sim 10\text{nm} \) [16]. All these studies indicate that the dry oxidation rate of the Si nanowires decreases due to the associated stress arising from the nonplanar viscous deformation of oxides, and that the retardation is more severe for smaller radii of Si nanowires and also more severe at low temperatures.

To the best of our knowledge, there have been any reports on the ramifications of the oxide layer coating on the optical phonon modes in Si nanowires. Here, we investigate both dry
and wet oxidation to make Si nanowires of \( d < 10 \text{nm} \), and discuss the ramifications of these processes on the optical phonons in Si nanowires.

### 7.2 Experimental Details

The two sets of PLV-VLS nanowires (Fe:Si) were prepared using two different oxidation routes. Using *in situ* dry oxidation process, the temperature of the growth chamber was first dropped to 900°C after growth at 1200°C, and dry oxygen was passed through the chamber at 100 torr and 100sccm for 1hr. The oven was cooled at 20°C/min under argon flow at the same rate as discussed in chapter 5. SiNWs were removed from the wall of the quartz tube for further analysis. In the *ex situ* oxidation process, the nanowires were removed from the PLV growth chamber under ambient conditions then oxidized in a second furnace under dry oxygen atmosphere at 900°C for 1hr. The sample was heated at 20°C/min under argon flow (100sccm, 100 torr) to 900°C for 1hr under dry oxygen flow. The furnace was cooled to ambient conditions at 20°C/min under argon flow as before. And the wires were collected for experiment.

High-resolution transmission electron microscopy (HRTEM) using a JEOL (JEM 2010F) microscope with a 100 kV accelerating voltage was used to observe the nanowire crystallinity and SiO\(_2\) coating. A JEOL (JEM 1200 EX) TEM operating at 120 kV was used to determine the diameter distribution for the nanowires. The TEM grids were prepared by suspending a small amount of nanowire material in ethanol, and an ultrasonic horn (Misonix Inc., #XL 2010) operated at 100 W was used to make a suspension.
7.3 Results and Discussion

In Figure 7–1a we show an HRTEM image of the Si nanowires oxidized \textit{in situ} Si nanowires. From the scale bar, we can see that the crystalline Si core ~ 5nm diameter is wrapped in a ~15nm oxide layer. It is expected that at such oxide layer thickness, oxide-induced strain on the Si core could be detected in the Raman spectrum. Strain causes the Raman band to shift to higher energy. However, no evidence of oxidative strain was observed in the Si nanowire. In Figure 7–3, we compare the 520 cm$^{-1}$ band of the bulk (bottom spectrum), \textit{in situ} oxidized, and \textit{in situ} oxidized and then wet etched in HF. Oxidation to produce a si core of 5 nm (HRTEM) has asymmetrically broadened the band to lower energy, characteristic of phonon confinement (the bulk spectrum is shown for comparison). The asymmetry is due to phonon confinement for three reasons: 1) the Raman spectrum was taken at very low laser flux (8\(\mu\)W/\(\mu\)m$^2$), 2) photo-thermal processes are negligible at this laser flux, as discussed in Chapter 6, and 3) the spectra was collected from a low wire density region with good thermal anchorage on the indium substrate. All these results indicate that, \textit{in situ} thermal dry oxidation can be used to produce small diameter si nanowires and at the same time prevents the formation and development of strain in the wires.
Figure 7–1: a) HRTEM images of an in situ dry oxidized Si nanowires before HF treatment. The nanowire has ~5nm crystalline core and ~15nm oxide coating.
Figure 7–2: b) HRTEM images of an in situ dry oxidized Si nanowires after HF treatment (10% HF, 2hrs), only ~3-4 monolayers of oxide coating remains. Lattice fringes of the crystalline core can be seen in both images.

Figure 7–1b is an HRTEM image of the in situ oxidized Si nanowires after HF treatment. HF is known to remove the SiO_x coating. The crystalline core is seen to be wrapped in a ~3-4 monolayer oxide coating. This coating likely formed after exposure to air. The Raman spectrum from the HF-treated nanowires is shown in Figure 7–3c. Three observations can be made when
comparing the Raman spectrum of the in situ oxidized nanowires and the HF-treated nanowires: 1) the spectrum from the HF-treated sample is downshifted to lower energy, 2) the HF-treated wire have larger linewidth, and 3) the HF-treated have larger asymmetry. After HF treatment the 518 cm\(^{-1}\) band of the as grown (in situ oxidized) downshifted \(\sim 1\) cm\(^{-1}\) with a \(\sim 25\%\) increase in the linewidth and a \(\sim 36\%\) increase in the asymmetry parameter. These data suggest that the phonon mode in the nanowire does extend through the oxide interface. The summary of the lineshape parameters is given in Table 7–1

Table 7–1: Comparison of the 520 cm\(^{-1}\) Si phonon parameters of in situ oxidized SiNWs (as grown) and HF-treated (\(\sim 3-4\) monolayer oxide layer). The data are from Figure 7–2.

<table>
<thead>
<tr>
<th></th>
<th>Peak Frequency (\omega_0) (cm(^{-1}))</th>
<th>FWHM (\Gamma) (cm(^{-1}))</th>
<th>Asymmetry Parameter (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In situ oxidized</td>
<td>518.7</td>
<td>8</td>
<td>1.1</td>
</tr>
<tr>
<td>(As grown)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF-treated</td>
<td>517.5</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>(c)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7–3: comparison of the 1st order Raman bands of the in situ dry oxidized SiNWs: a) the bulk Si spectrum, b) in situ oxidized (as-grown), and c) the HF treated.

Now we examine results from the ex situ dry oxidation of SiNWs. The HRTEM images of Si nanowires are shown in Figure 7–4. The as grown nanowire (Figure 7–4a) are large i.e., d ~45nm crystalline core with a ~ 5nm oxide coating. After the dry ex situ oxidation, we see a thick oxide coating ~20nm and a small crystalline core ~8nm as shown in Figure 7–4b. Figure 7–4c is an HRTEM image of an ex situ oxidized wire after HF treatment. The Raman spectrum of these three samples is shown in Figure 7–7. We observed an upshift ~ 1 cm\(^{-1}\) in the Raman spectrum of the ex situ oxidized sample compared to the as grown sample, characteristic of oxide induced strain upshift.
Figure 7–4: a) HRTEM images of SiNWs before dry oxidation (as grown). The wire has ~5nm oxide coating and ~45nm crystalline core.
Figure 7–5: HRTEM images of *ex situ* oxidized SiNWs after dry oxidation. The crystalline core is ~8nm with ~20nm oxide coating.

We attribute this upshift to the strain induced by the thick oxide layer. The lineshape is also narrower compared to the as grown. This may be due to the annealing. However, after removing the oxide layer by HF treatment, we observed a downshift to lower energy and a slight asymmetry develops associated with phonon confinement.
Figure 7–6: HRTEM images of \textit{ex situ} oxidized SiNWs after HF treatment of sample b.
Figure 7–7: 1st order Raman band of *ex situ* oxidized Si nanowires comparing the lineshapes of the as grown, after *ex situ* oxidized and HF treated Si nanowires. The wires were deposited with low density on In substrate and excited with 514.5 nm radiation at 8µW/µm².
It is not clear why the HF treated increased the line asymmetry. It could be that the average wire diameter decreased as the result of the HF treatment (i.e., HF is known to etch Si as well. The details of the lineshape parameters is shown in Table 7–2

<table>
<thead>
<tr>
<th></th>
<th>Frequency $\omega_o$ (cm$^{-1}$)</th>
<th>FWHM $\Gamma$ (cm$^{-1}$)</th>
<th>Asymmetry Parameter $A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-grown</td>
<td>519.7</td>
<td>7.5</td>
<td>1.1</td>
</tr>
<tr>
<td>ex situ oxidized</td>
<td>521</td>
<td>6.5</td>
<td>1.2</td>
</tr>
<tr>
<td>HF treated</td>
<td>517</td>
<td>8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

It is evident that the nature of the oxidation process has a measurable effect on the phonon modes. this work has also demonstrated that, in situ thermal oxidation will be the best route in oxidation process if strain is not desirable.

7.4 Conclusions

We have demonstrated that dry oxidation in 100 torr O$_2$ at 900° C can be used to produce smaller diameter Si nanowires, e.g. 5 nm diameter crystalline cores wrapped by 15-20 nm of oxide. The oxide can then be removed by an HF etch. The Raman spectrum (520 cm$^{-1}$) band is sensitive to the processing, showing diameter decrease via phonon confinement and oxide-induced upshift in
the band position (strain). This work has demonstrated that *in situ* oxidation is the best oxidation process to produce strain free Si nanowires, thus, *in situ* oxidation is preferred as it seems to avoid compressive strain. Further work is needed to test this work on a more quantitative footing.
REFERENCES

Chapter 8

Fano Resonance Scattering in Crystalline Ge Nanowires

8.1 Introduction

Raman scattering studies have been carried out on $d \sim 8$ nm diameter Ge nanowires as a function of laser flux. Using the Stokes/AntiStokes scattering intensity ratio for the phonon modes we have estimated the local sample temperature induced by the incident laser flux ($\Phi$) and find almost a linear relationship $\Phi \sim T$. We also observed that the phonon lineshape is flux dependent and is possibly a Fano interference lineshape. In this work, we present results from a systematic set of similar experiments on small diameter Ge nanowires. Similar to what we discussed in previous chapters for SiNWs, we find that Fano resonance scattering can develop in Ge NWs with increasing laser flux. Even though our Ge NWs presumably make physical and thermal contact to the substrate (indium foil), the NW temperature is easily driven upward to $\sim 800$ K at 6.37 mW/$\mu$m$^2$ incident laser flux (488 nm), as determined from the Stokes/Anti-Stokes intensity ratio. This temperature increase will be shown to drive the Fano resonance lineshape parameters.
8.2 Experimental Details

Ge nanowires were prepared by pulsed laser vaporization (PLV) [1] of a Ge target containing ~ 10 at. % of Au. The target (12 mm in diameter, 8 mm thick) was prepared by uniaxially pressing (10,000 psi) well-mixed ~0.8-1.5 micron diameter 99.999% pure Ge and Au powders (Alfa-Aesar Inc.). The target was centered in a 25 mm diameter quartz tube located in a 1 m long tube furnace. The target was positioned approximately at the middle of the furnace facing the incoming laser beam. The target was heated to 830°C, as determined by an inconel-sheathed N-type thermocouple placed just behind the target. Preheated, ultra high purity Argon gas (99.999%) was passed down the axis of the quartz tube at 100 sccm, in the same propagation direction as the incident beam from a pulsed Nd:YAG laser (10 Hz repetition rate; Spectron Laser System, Model SL803) [2]. Laser pulses at the fundamental (1064 nm, IR) and the harmonic (532 nm, vis) were focused to the same spot on the target (~2mm spot size), at a pulse energy of 950 mJ/pulse (1064nm) and 320 mJ/pulse (532nm). The laser (diameter~ 2mm) was then rastered across the surface of the target using a computer-controlled lens. The fundamental IR pulse was delayed by 50 ns with respect to the visible harmonic pulse. The short duration (~6ns), high intensity pair of laser pulses caused a vapor plume of Ge and Au to be ejected normal to the target. The gas flow is used to reverse the direction of the plume leaving the target, and the NWs were found to deposit on the tube wall behind the target at a position where the temperature was ~500°C. The Ge NWs studied here were removed from the wall of quartz tube for study. The samples for Raman scattering studies were prepared by making a short-lived suspension of NWs in ethanol using ultrasound. A few drops of this solution was placed on a substrate and allowed to evaporate under ambient conditions.
High-Resolution Transmission Electron Microscopy (HRTEM) using a JEOL 2010F electron microscope with a 100 kV accelerating voltage was used to observe the nanowires crystallinity and oxide coating. TEM sample grid (Lacey Carbon, EMS) were prepared by suspending a small amount of nanowire sample in ethanol, using an ultrasonic horn operated at 100 W (Misonix Inc., #XL 2010) for 10 min. Shown in Figure 8–1 is the HRTEM image of Ge NW with a 9nm diameter crystalline core and ~2 nm oxide coating. The high contrast <111> lattice image planes appear parallel to the growth direction, suggesting a <110> growth axis. This is confirmed by the selected area diffraction (SAD) pattern shown as inset (ii) in Figure 8–1. Also shown as inset (top left) is the diameter distribution from TEM images, analyzed using the image analysis software (NIH image software; http://rsb.info.nih.gov/nih-image). The solid line is a least squares fit of a log-normal distribution to the data (d_{ave}~8 nm, σ~1.5) [3].

Raman spectra were collected with the sample substrate at room temperature in the backscattering configuration using a JY-ISA Horiba T64000 spectrometer equipped with a cooled CCD. The spectral resolution of all data here is ~ 1.5 cm\(^{-1}\). An Olympus BX40 confocal microscope was used to illuminate a ~ 1μ diameter focal spot size at the plane of the sample and collect the backscattered light. An Argon ion laser was used to excite the sample, and the flux Φ at the sample was varied in the range 0.07mW/μm\(^2\) ≤ Φ≤14.00mW/μm\(^2\), as measured at the sample position using a miniature, hand-held radiometer. Unpolarized Raman spectra were collected in air using 488nm excitation. The laser flux was used to control the temperature in the scattering volume of the nanowires.
Figure 8–1: HRTEM of Ge nanowires. The \{110\} lattice planes and the (110) directions are parallel and perpendicular to the growth axis respectively, with the \{111\} planes at 45° to the \{110\} planes, suggesting a (001) growth direction. The inset (ii) is SAD of the same wire depicting \{110\} planes diffraction pattern with (001) zone axis. The histogram (top left) is the diameter distribution with a log-normal fit to 8nm most probable diameter.

8.3 Results and Discussion

In Figure 8–2, we display the Stokes (S) and Anti-Stokes (AS) Raman bands for the LO-TO zone center mode of the Ge NWs. Both the S and the AS bands were collected simultaneously (i.e., without any optical changes in the system). The spectra are stacked in the figure, with the lowest excitation power spectrum on the bottom (0.07mW/\mu m^2), and the highest
excitation flux spectrum at the top (8.42~ mW/µm²). The ratio of the Anti-Stokes (AS) to Stokes (S) integrated intensities is related to the local sample temperature $T$ by [4]

$$\frac{I_{AS}}{I_S} = A \exp\left(-\frac{\hbar \omega_p}{kT}\right), \quad (8.1)$$

where $A$ is a dimensionless normalization constant that depends on the optical absorption constant, the scattering cross section and Raleigh factor for the Stokes and AntiStokes scattering (see chapter 4), $k$ is Boltzman constant, $\omega_p$ is the peak frequency of the Raman band and $T$ is the absolute temperature. Using equation 8.1 and the spectra of Figure 8–2, we can correlate the local temperature in the Ge nanowire with the laser flux. The result is shown in Figure 8–3, where we plot the local temperature in the scattering volume ($T$) vs. the incident laser flux ($\Phi$). As can be seen from the figure, the local temperature, as determined from the Stokes/Anti-Stokes ratio, is approximately linear in the incident laser flux. In Figure 8–2, we see that increasing laser flux causes the Stokes and AntiStokes bands to develop a noticeable increasing asymmetry with the bands broadening to lower frequency. In bulk intrinsic Ge, this Raman band exhibits a Lorentzian lineshape [5]. Richter [6], and later Campbell and Fauchet [7] showed that asymmetric Raman lineshapes can develop in small diameter semiconducting q-dots and nanowires. Therefore, the issue of asymmetry in the S and AS LO-TO Raman bands of our Ge NWs is of fundamental importance.
Figure 8–2: Flux dependence of the Stokes and AntiStokes lineshape of Ge nanowires of d = 8nm diameter on an Indium foil substrate. The spectra were collected with the 100X objective (~1µ spot size). The Raman bands downshift to lower energy and asymmetrically broadened to lower energy with increasing flux.
Figure 8–3: Dependence of local sample temperature (as determined from the stokes/Antistokes intensity ratio) on the incident laser flux. The plot exhibits a linear dependence. The solid line is a guide to the eye and the shaded region represent an onset of sample morphological changes.

For the specific case of Ge, we show in Figure 8–4 a comparison of the Raman band shape for bulk Ge (dashed line) and nanowire Ge (solid line), where the latter is calculated according to equation 5.9 using $\Gamma = 5.0 \text{ cm}^{-1}$, $D_o = 8 \text{ nm}$ (the mean crystalline core diameter of the nanowires in our sample) and using the LO phonon dispersion obtained from neutron scattering [8]. Weak asymmetry consistent with the RCF model $D_o \sim 8 \text{ nm}$ is evident in the figure.
As we have shown in previous chapters, a Fano resonance can have a similar lineshape to that from phonon confinement, although the physics behind the Fano lineshape is completely different from the RCF lineshape (phonon confinement). Of course, for the RCF model to be valid, it is required that the phonon mean free path must be comparable to, or greater than, the nanowire diameter. In this regard, using the full width at half maximum (FWHM) of the Raman band as a measure of the phonon lifetime, we find that the phonon mean free path is approximately a factor $\sim 2$ shorter in the nanowire than in bulk Ge, i.e., the FWHM in the bulk is $\sim 1/2$ that in the nanowires.

Figure 8–4: Comparison of a Lorentzian lineshape (dashed lines) of the bulk to 8nm Ge nanowire (solid line) using equation 5.9.
Fano interference scattering process has been observed in many occasions in doped bulk semiconductors [9]. For example, in p-doped Si and p-doped Ge, the lineshape of the Raman-active mode asymmetrically broadens to higher energy, whereas in n-doped Si and Ge, the lineshape broadens asymmetrically to lower energy.

We now return to the laser flux driven Fano lineshape data (shown in Figure 8–2). In order to produce the Fano Resonance effect, the energy of the discrete Raman-active phonon mode should overlap with energy continuum of the Raman-active electronic transitions. In Ge, this interference process can be achieved by inter-conduction band or inter-valence band transitions. The observed experimental results in this work suggest only inter-conduction band transition, since the lineshape broadens to lower frequency. As has been pointed out in other reports [10], the elastic properties of semiconductors depend on the free electron or hole concentration. Any perturbation that causes dynamic carrier redistribution among the energy bands in the semiconductor will result in the “softening” of the lattice and thus a change in the phonon frequency. However, no frequency change was observed even at 350°C[9] for n-doped bulk Ge. This was attributed to short interband scattering time in which the electrons had insufficient time to redistribute themselves in the bands in one period of a lattice oscillation, and therefore make no contribution to the \( \bar{q} \approx 0 \) optic phonon frequency. The negative \( \alpha \) we find for the Fano Resonance strongly suggests interconduction band transition suggesting that our wires may be doped. It should be recalled that in the limit of weak coupling \( (1/\alpha \to 0) \), the Fano line shape is a Lorentzian. We consider our lowest excitation power data first (bottom trace Figure 8–2). Shown in Figure 8–5 is the Stokes experimental data (open circles) which has been fitted with both a Lorentzian line shape (dotted line; eq. 2 with \( 1/\alpha=0 \)) and a Fano resonance (solid
line, eq. 2) where all the Fano parameters \((I_0, 1/\alpha, \Gamma, \omega_0)\) are free parameters in the least squares fit. The two curves below represent the difference between the experimental and calculated lineshape for the case of Fano (solid) and Lorentzian (dashed) functions. Even though the Fano line shape fits slightly better, it may not appear very convincing at this point that the Fano interference mechanism should be invoked, which also suggest that the lineshape is still asymmetric at low power. However, the case becomes stronger when we consider all the data collected as the sample temperature is driven higher by higher excitation flux.

In Figure 8–6, we display the inverse of asymmetric parameter peak frequency and linewidth as a function of temperature (bottom scale) and flux (top scale). In one case (\(\Delta\)), we checked the sample damage threshold by recording data at the lowest flux (~0.07 \(\mu W/\mu m^2\)) after recording the data at each flux. For the solid dots, crosses, and crossed triangle, we kept increasing the laser power and collected the S/AS spectra. The solid line in the figure represents a guide to the eye. The solid squares are the flux dependent data. Most importantly, the data can be extrapolated smoothly to a non-zero value for the Ge NW samples at the lowest flux which does not significantly raise the temperature of the sample. In other words, we feel confident in assigning a small asymmetry to the lowest flux data. We observed a shape increase in asymmetry at temperatures above ~ 800K. We believe this may be due to strong coupling and transitions to higher energies since the coupling parameter is known to increase with increasing carrier concentration [9].
Figure 8–5: Comparison of a Fano fit and Lorentzian fit to the least flux data. We see a small deviation in the Lorentzian fit. The two curves below represent the difference between the experimental and calculated lineshape for the case of Fano (solid) and Lorentzian (dashed).
Figure 8–6: Variation of asymmetry parameter, linewidth and frequency with temperature (solid circles and triangles) and flux (solid squares) All lineshape parameters exhibit exponential dependence to ~800K
As will be explained later, the Raman band of annealed sample upshifts in energy with respect to the as grown sample. As have been observed in annealed samples, the upshift increases with increasing laser flux (as shown in Figure 8–7) or thermal annealing temperature. Thus, it is expected that the relation between $\omega_0$ and $T$ to be linear as in the bulk, but the contribution from the laser annealing is significant causing the observed nonlinearity.

Returning to Figure 8–6, at large enough laser flux, the sample is irreversibly heated, i.e., the low T lineshape is not recovered. It should be recalled that the sample are measured in air and are likely oxidized. Depending on the specific sample and experimental conditions, the threshold flux at which irreversibility occurs is different. A reversibility test was done to check the damage threshold of the NW sample. As explained earlier, after a spectrum at each higher laser flux, another spectrum was taken at the lowest laser flux (0.07mW/µm$^2$) for comparison to the original spectrum at that flux. As can be inferred from Figure 8–2, there is a sudden increase in $\omega_0$ and $\Gamma$ above the 2.5mW/µm$^2$ spectrum. We believe this is onset of irreversible changes (possibly by oxidation) as a result of laser heating in air. We attribute the gradual increase in the peak energy and linewidth as due to the coupling of the optical phonon and laser produced electrons participating in the Raman scattering. The irreversibility becomes significant at high laser flux. At 14.00mW/µm$^2$ laser flux, we observed a permanent upshift to higher energy in the Raman band. This is a signature of annealing in vacuum or Ar, but what is happening here is not yet clear.
Our annealing hypothesis was confirmed by Raman Spectrum from the same batch of samples which was thermally annealed at 900K in vacuum and argon. We observed a 1.5 cm$^{-1}$ upshift in the 0.07mW/µm$^2$ spectrum after taking the 14.00mW/µm$^2$ spectrum. Shown in Figure 8–7 is the comparison of the Raman spectra at 0.07mW/µm$^2$ after collecting spectrum at
2.50mW/µm² (open circles) and 14.00mW/µm² (solid line) and the original data at 0.07mW/µm² (+ signs). It is clear that the process is reversible at 2.50mW/µm², and highly irreversible at 14.00mW/µm². We observed that, apart from the laser flux, such changes depend on the collection time of Raman spectra.

8.4 Conclusions

In conclusion, we have observed a Fano interference process in Ge nanowires driven at high laser flux. The origin of the interference is probably the coupling between the discrete (300 cm⁻¹) phonon and an electronic continuum generated by the laser. It is curious that similar behavior with laser flux is observed with Si and Ge nanowires as the sign of the doping, n- or p-, would have to be the same. It is possible that both Au (in Ge) and Fe (in Si) can produce electrons in the conduction band with an assist from the laser. Further work at low temperature and on isolated nanowires will hopefully provide more insight into mechanism helping the Fano resonance in Ge nanowires.
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Chapter 9
"Twinning Superlattice" in GaAs Nanowires

9.1 Introduction

Conventionally, there are three types of superlattices that have been grown in thin films: modulation of the atomic stacking periodicity, modulation of the material composition or modulation of the doping. All these structures are said to be highly vulnerable to interface degradation due to lattice mismatch and the incoherent scattering of carriers trying to propagate normal to the film as a result of dangling bonds or surface roughness in the vicinity of the interface. In twinning superlattices these problems can be mostly overcome. Twinning superlattice is based on periodic reversal of the atomic planes stacking sequence in the structure. These changes in the stacking period can produce significantly different properties in the superlattice from the bulk. Theoretical investigations of the electronic band structure of a twinning superlattice materials reveals a red shift in the semiconducting band gap [1,2].

We have used a simple thermal batch process to grow GaAs nanowires. Our growth conditions lead to an almost periodic twinning superlattice. From HRTEM, we observed that the superlattice period decreases with increasing diameter, in $d = 30$ nm with a typical period having ~5 unit cells along the (111) direction. Hibini and Ogino[3] were the first to report the synthesis of 2D twinning superlattice in thin films. However, as far as we know, there are no reports on twinning superlattice of 1D or quasi 1D structure. In this work, we report our studies
on twinning superlattice of GaAs nanowires. Our studies reveal what appears to be quantum confinement effects associated with the superlattice period. To the best of our knowledge, this is the first report on twinning superlattice nanowires.

9.2 Experimental Details

The GaAs twinning superlattice nanowires were synthesized by a thermal batch process in which a pellet of Au$_{0.1}$GaAs$_{0.9}$ is simply heated in an argon gas stream. The pellet was prepared by uni-axially pressing a mixture of GaAs and Au powder (Alfa Aesar, 99.999%). The pellet was mounted in a quartz tube centered inside a tube furnace. The growth was done at 1200°C in Argon at 100sccm flow rate and 100 Torr pressure. No laser radiation was used in this synthesis approach which is a thermal batch process (TBP). The growth chamber is shown in Figure 9–1.

For HRTEM and Raman characterization, part of the sample collected from the synthesis chamber (~ 6.0" behind the pellet) was suspended in ethanol using an aquasonic (VWR, model P250HT) for 30min, and then further sonicated with an ultrasonic horn (Misinix Inc. model #XL 2010) operated at 100W. High-Resolution Transmission Electron Microscope (HRTEM) using JOEL (JEM 2010F) microscope with a 100kV accelerating voltage was used. A drop from the suspension was used to prepare the TEM grid (Lacey Carbon, EMS).
Figure 9–1: The growth chamber of the thermal batch process (TBP) showing the in situ gas heating configuration. The growth pressure ranges (100-700Torr) and temperature ranges from 1073K-1473K

The Raman scattering spectra were collected at room temperature in the backscattering geometry using a JY-ISA T6400 micro-Raman spectrometer, operating at ~ 1µ diameter focal spot size at the plane of the sample. An Argon ion laser was used to excite the spectra. The spectra were collected in air under ambient conditions using the 488nm line.

9.3 Results and Discussion

The nanowires grown by the TBP have diameter ranging from 30nm to 100nm as determined by TEM. In Figure 9–2a we show the selected area diffraction (SAD) recorded perpendicular to the nanowire axis. The diffraction pattern shows a [111] growth axis of a twinned fcc crystal lattice of GaAs. The growth direction of our GaAs nanowires is the same as that reported in the laser assisted growth process [4,5]. However, this work did not report the
presence of twin formation. In Figure 9–2b, we show the lattice planes of a d = 32nm wire which shows a high density for twining with 180° rotation about the [111] direction of the zinc-blende structure. This image is consistent with the SAD in Figure 9–2a. In Figure 9–2c, we show the TEM of the twinning bands of ~100nm diameter nanowire. The periodicity of the twin bands is very distinctive, with each band ~20nm in length. We observed that smaller diameter wires exhibit a higher density of twinning. The main factors behind the formation of the twin superlattice are not known. It may be the ratio of Ga to As at the growth interface [6-9], or the surface energy at the growth interface [7-9] and the type of facets [10] that are developed during the growth process. Compositional analysis (EDX) from three different spots (see Figure 1d) in the same wire is shown in Figure 9–3. Spots 2 and 3 reveal ~ 4% Ga-rich nanowires suggesting a p-type nanowire. Contrary to the report in ref. 10, our analysis of the growth tip of the nanowire (spot 1) shows the presence of only Au and Ga (no As) suggesting that a GaAu liquid droplet drives the vapor-liquid-solid (VLS) growth process. However, after the growth stops, it may be that As either evaporates from the droplet or diffuses into the wire near the growth tip. The absence of twins in the GaAs nanowires produced by pulsed laser vaporization, and the absence of As in the tip of the wire suggest that Ga:As ratio fluctuations can play an important role during the twinning formation.
Figure 9–2: a) SAD pattern of GaAs twinning superlattice nanowire showing the twinning along the[111] direction., b)HRTEM of GaAs twinning superlattice nanowire showing the 180 twin orientation, indicative of the twinning superlattice., c) TEM image of ~100nm twinning superlattice GaAs nanowires with ~20nm twin periodicity. d) shows 3 different spots for EDX. The spectra is shown in Figure 9–3.
The VLS growth process is limited by the diameter and the surface energy of the initial cluster in the liquid phase, the effective chemical potential of the equilibrium phases and the supersaturation conditions of the initial nano-cluster in the liquid phase. For this reason, one might expect that the Ga:As ratio could fluctuate frequently in smaller wires, leading to a higher twin density in these wires.

*Figure 9–3*: EDX from 3 different spots on the nanowire shown in Figure 1d. Spot 1 (growth tip) clearly shows As deficiency.
A variety of optical techniques has been developed to study impurities and intrinsic point defects in III-V semiconductors. Among these experimental techniques are photoluminescence, infrared absorption and Raman spectroscopy. Other techniques includes photoconductivity, photo hall effect and deep level transient spectroscopy (DLTS) [11]. The point defects can be introduced into the semiconductor by nonstoichiometric growth process or by ion/neutron bombardment/implantation. In GaAs, the arsenic vacancy $V_{As}$ is identified to be a donor with energy at 45 meV below the conduction band [12,13]. The arsenic and gallium interstitials As, and Ga, are also expected to be donors, but the gallium vacancy $V_{Ga}$ is expected to be an acceptor [14,15]. The arsenic antisite $As_{Ga}$ has been identified to be at midgap level [16], whereas the energy of the gallium antisite $Ga_{As}$ has been placed at 78 meV above the valence band [17,18]. The ionization energy of the acceptor defect $V_{Ga}$ was determined to be $42.2\pm0.3$ meV above the valence band[18]. The gallium vacancy ($V_{Ga}$), gallium antisite ($Ga_{As}$), and arsenic antisite ($As_{Ga}$) have been identified by photoluminescence (PL) spectroscopy, whereas arsenic vacancy ($V_{As}$) by deep level transient spectroscopy (DLTS)[11]. Another technique that has been used to study native impurities and intrinsic point defects in GaAs is Electronic Raman Scattering (ERS). ERS has been used to identify both residual and intrinsic acceptors in GaAs [19]. The ERS spectrum of the residual shallow acceptors Carbon and Zinc has been observed at 122 cm$^{-1}$, 148 cm$^{-1}$, 155 cm$^{-1}$, 172 cm$^{-1}$ and 153 cm$^{-1}$, 174 cm$^{-1}$, 184 cm$^{-1}$, 203cm$^{-1}$ respectively in GaAs has been reported[11,19,20]. Extensive investigation of ERS of p-type Ga-rich GaAs has established the energy of the doublet acceptor (78 meV) to occur at 511 and 540 at 6K. It is reported that these bands disappear at temperatures above 50K [20], indicative of their electronic nature.
Our GaAs nanowires are expected to be Ga-rich, since the growth process was at 1200°C. This is the case because the arsenic vapor pressure is five orders of magnitude [21] greater than that of gallium at the 1200°C growth temperature, and with the constant flow of Ar gas in the growth system, nonstoichiometric gallium rich nanowires are expected. This is confirmed by the EDX shown in Figure 9–3, where ~4% Ga-rich wires are found. With this background, let us consider the Raman spectrum of our nanowires. Shown in Figure 9–4 is the Raman spectra of the twinning GaAs nanowires in comparison with the bulk. The zone center LO-TO phonon peaks of the nanowire are weakly asymmetrically broadened to lower energies and both the LO (288.4 cm\(^{-1}\)) and the TO (265.4 cm\(^{-1}\)) peak frequencies are downshifted by ~3 cm\(^{-1}\) and 2 cm\(^{-1}\), respectively, as compared to the bulk; (LO, 291.6 cm\(^{-1}\); TO, 267.4 cm\(^{-1}\)). The observed downshift and asymmetric broadening in both LO and TO, are tentatively attributed to the twin boundaries as they have a period much less than the wire diameter. Detailed study of these observed effects in the optical modes is under way.

Contrary to our results, ref. 12 reported a downshift of approximately 40 cm\(^{-1}\) in only the LO mode of a conventional GaAs nanowire. This was attributed to impurities, defects and stress in the nanowires. Just recently, Mahan and coworkers [22] have shown that the downshift in only the LO mode is due to a “shape effect” i.e., a reduction in the splitting between the LO and TO modes in polar semiconductor that arise from the long range dipolar interaction within the nanowires. They showed that the reduction in the LO-TO splitting depends on the aspect ratio of the nanowires [23]. In addition to the LO, TO zone center optical phonon modes, we observed a strong peak at 515 cm\(^{-1}\). This peak can not be identified with any Raman bands that has been observed in the bulk GaAs [24] or p-type Ga-rich GaAs [19,20]. The peak frequency 515 cm\(^{-1}\) is
not $2 \times \text{LO}$, or $2 \times \text{TO}$ or $\text{LO} + \text{TO}$ in frequency either. Thus, we believe that this peak may be a characteristic feature of the twinning superlattice period.

Figure 9–4: Raman spectra of GaAs twinning superlattice nanowires (top) in comparison with the bulk GaAs (bottom). Apart from the intrinsic LO-TO modes observed in the twinning superlattice nanowire spectrum, there is a strong peak at 515 cm$^{-1}$, which is attributed to the twinning in the nanowires.

Now let us turn our attention to the PL spectrum shown in Figure 9–5. Theoretical investigation [2] on the optical properties of the twinning superlattice predicts a red shift in the band gap. In our PL studies of the twinned superlattice GaAs nanowires, we observed a small red
shift of the bandgap PL peak, i.e., at 1.35 eV (nanowire) compared to the 1.42 eV of the bulk, at room temperature. In addition, the weak peak at 1.29 eV may be an excitonic peak, which is ~60 meV below the PL peak at 1.35 eV. This is about 10 times that of the bulk (5.3 meV) at room temperature. The 1.29 eV peak is also possibly associated with donor state to valence band luminescence. We also observed a peak at 2.14 eV. The twinning bands in our nanowires ranges from 2nm to 20nm, which is comparable to the excitonic Bohr radius of GaAs ~ 12.5nm. So it is possible that the exciton is modified by the superlattice.

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*Figure 9–5*: Photoluminescence (PL) of twinned superlattice GaAs nanowire at 30K (thin solid line) and 300K (thick solid line). Structures in the nanowire PL occur at 1.29eV, 1.35eV and 2.14eV. The bulk has bandgap PL at 1.42 eV at room temperature.
9.4 Conclusion

In conclusion, we have used a thermal batch process of a Au/GaAs pellet to make twinning superlattice nanowires. We observed a red shift in the bandgap luminescence. In the Raman spectrum, we observed LO and TO bands slightly downshifted (~ 3 cm\(^{-1}\)) relative to the bulk. However, a very strong peak at 515 cm\(^{-1}\) is observed that is not seen in the bulk. This is identified with the superlattice and is either a second order feature or electronic scattering. The temperature dependence of the 515 cm\(^{-1}\) should be measured to learn if it is electronic Raman or a second order (2-phonon) peak. Such wires will overcome the difficulty in making very small wires to observe quantum confinement effect and possibly can be used to study quantum interferometric effects. Such wires might also be good candidate for IR detection. Also, we have identified a strong peak at 515cm\(^{-1}\) and have attributed it to the twinning superlattice.

Further work is required to authenticate this important observation also to develop a controllable approach for synthesizing such nanowires. We believe that a controlled growth of such wires may have an immense impact on electronic nano-device technology.
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Selected Publication