8-2007

Laser-assisted synthesis and optical properties of bismuth nanorods

Jason Reppert

Clemson University, jrepper@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_theses

Part of the [Materials Science and Engineering Commons](#)

Recommended Citation

Reppert, Jason, "Laser-assisted synthesis and optical properties of bismuth nanorods" (2007). *All Theses*. 188.
https://tigerprints.clemson.edu/all_theses/188

This Thesis is brought to you for free and open access by the Theses at TigerPrints. It has been accepted for inclusion in All Theses by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.

LASER-ASSISTED SYNTHESIS AND OPTICAL PROPERTIES OF
BISMUTH NANORODS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Jason Brooks Reppert
August 2007

Accepted by:
Dr. Apparao M. Rao, Committee Chair
Dr. Kathleen Richardson
Dr. Jian Luo

ABSTRACT

Bismuth in the bulk form is a semimetal with a rhombohedral structure. It has a small band overlap between the conduction and valence bands and a highly anisotropic electron effective-mass tensor. Thermoelectric materials, in which one of the three dimensions is in the nanometer regime, exhibit unique quantum confinement properties and have generated much interest in recent years. Theoretical investigations have suggested that nanowires with diameters <10 nm will possess a figure-of-merit $ZT > 2$. Prior to this research, it has been shown by the Dresselhaus group at MIT that Bi nanowires with small enough diameters (~ 50 nm), prepared via the template-method, undergo a transition from a semimetal with a small band overlap to a semiconductor with a small indirect band gap. Infrared absorption, temperature-dependent electrical resistance and magneto-resistance measurements were used to confirm this semimetal-to-semiconductor phase transition.

In this thesis, we report the synthesis of ~ 10 nm diameter Bi nanorods using a pulsed laser vaporization method that was previously developed for preparing single-wall carbon nanotubes. The high resolution transmission electron microscopy images of our Bi nanorods show a crystalline Bi core oriented along $\langle 012 \rangle$ direction, and coated with a thin amorphous bismuth oxide layer. The infrared absorption and the surface plasmon peaks in our Bi nanorods are blue-shifted in energy when compared to the corresponding spectra in bulk Bi, and relative to those reported by the Dresselhaus group in 45 – 200 nm diameter Bi nanowires.

DEDICATION

I want to dedicate this thesis to my belated grandfather, Philip L. Bitely. Without your wisdom and meaningful teaching of valuable life skills, I would not be the person I am today. You are deeply missed.

ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Dr. Apparao M. Rao for his guidance, help and friendship over the past couple of years. Not only has he taught me the techniques needed to succeed in the lab, but he has also offered valuable lessons about life. Next, I recognize that some of the work and ideas done in this thesis would not have been possible without the meaningful insights given to me through various discussions with Dr. Malcolm Skove and Dr. Jian He. In addition, I would also like extend thanks to my lab mates for their guidance and friendship.

Finally, I would like to thank my parents and loving girlfriend for supporting me through the years. Without their love and support, I would not be where I am today.

TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER	
1. INTRODUCTION	1
1.1 Figure of Merit	5
1.2 Seebeck Effect	7
1.3 Peltier Effect	10
1.4 Thomson Effect	12
1.5 Density of States	13
2. BACKGROUND AND THEORY	15
2.1 Semimetal-to-Semiconductor Transition	19
2.2 Quantum Confinement	23
3. SYNTHESIS TECHNIQUES	27
3.1 Template-Based Synthesis	27
3.2 Chemical Vapor Deposition	29
3.3 Hydrothermal Method	31
3.4 Thermal Evaporation	33
3.5 Pulsed Laser Vaporization	34
3.6 Growth Mechanisms	36

Table of Contents (Continued)

	Page
4. EXPERIMENTAL METHODS, RESULTS AND DISCUSSION	40
4.1 Electron Microscopy	40
4.2 FTIR Spectroscopy	44
4.3 UV-Visible Spectroscopy	56
5. SUMMARY	62
5.1 Conclusions	62
5.2 Future Work	63
REFERENCES	64

LIST OF TABLES

Table		Page
4.1	Calculated effective mass components of each carrier pocket for determining the band structure in Bi nanowires at 77 K along the indicated crystallographic directions, based on the effective mass parameters of bulk Bi. The z' direction is chosen along the wire axis and all mass values are in units of the free electron mass, m_o	52

LIST OF FIGURES

Figure		Page
1.1	Temperature dependence of ZT of $10\text{\AA}/50\text{\AA}$ p -type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice compared to those of several recently reported materials.....	3
1.2	Predicted ZT of Bi nanowires. As the nanowire diameter decrease, the ZT increases. When diameter reaches ~ 10 nm, the ZT is predicted to be ~ 2	5
1.3	The figure of merit as a function of temperature for a variety of bulk TE materials.....	7
1.4	Schematic of a conductor showing electrons (or holes) diffusing from the hot end (T_H) to the cold end (T_C).....	8
1.5	Schematic of a TE couple made of an n -type and p -type semiconductor material. A temperature gradient is applied across the device and a direct conversion of heat into electrical power is achieved.....	9
1.6	Schematic of the Peltier effect showing a current flowing through two different materials. At the junction, heat is produced which can be used as energy	11
1.7	Schematic of a TE couple made of an n -type and p -type semiconductor material. A current is passed through the two materials, heat is absorbed and then rejected as cool air.....	12
1.8	Schematic of the Thomson effect. A current flows through the material and a temperature gradient is applied to it, thus thermal energy is created.....	13
1.9	Electronic density of states for 3D bulk materials, 2D quantum well, 1D quantum wire and 0D quantum dot	13
2.1	(a) Bismuth crystal structure showing 4 unit cells. Z -axis is pointing upward. (b) Hexagonal pattern created by the trigonal symmetry of Bi. Z -axis is pointing out of the page Four-band model of bulk Bi with energy gaps E_{gL} and E_{gT} at the L -point and the T -point of the Brillouin zone, respectively.....	17

List of Figures (Continued)

Figure	Page
2.2 The Brillouin zone of Bismuth.....	18
2.3 Schematic diagram of the Bi band structure at the L -points and T -point near the Fermi energy level, showing the band overlap, E_0 , of the L -point conduction band and the T -point valence band. The L -point electrons are separated from the L -point holes by a small band gap E_{gL} . At $T = 77$ K, $\Delta_0 = 38$ meV and $E_{gL} = 13.6$ meV	19
2.4 Schematic diagram of the Bi nanowire semimetal-to-semiconductor transition. The lowest conduction sub-band (L -point) moves up in energy and the highest valence sub-band (T -point) moves down in energy	21
2.5 Calculation of the lowest T -point and highest L -point sub-band energies as a function of wire diameter at 77 K.....	22
2.6 Calculated band gap energy versus radius for ZnO nanoparticles based on the effective mass model.....	24
2.7 Plot of the predicted band gap energy as a function of nanorod diameter based on the modified effective mass model for Bi nanorods	26
3.1 3D representation of the alumina template method	28
3.2 Left: SEM image of the porous alumina anodic layer with ~ 40 nm pore diameter. Right: SEM image of Bi nanowire array after the template has been filled with Bi.....	29
3.3 Schematic of the CVD method used to prepare a variety a nanomaterials	30
3.4 SEM image of Germanium nanowires synthesized by CVD.....	31
3.5 Schematic of the hydrothermal/solvothermal method used for producing nanomaterials	32
3.6 TEM image of the as-synthesized ZnO nanobelts by thermal evaporation	33
3.7 Schematic representation of our pulsed laser vaporization setup	34

List of Figures (Continued)

Figure	Page
3.8	TEM image of Si nanowires produced by the PLV method from the Si _{0.9} Fe _{0.1} target. The material was collected from the cold finger and the arrows indicate the catalyst particle..... 36
3.9	Proposed VLS growth mechanism for Si nanowires 37
3.10	Pseudo-binary phase diagram for GaAs and Au. The liquid Au-Ga-As component is represented as L..... 38
3.11	Binary phase diagram for Bi and Au..... 39
4.1	TEM image of the as-prepared Bi deposit obtained from a pulsed laser vaporization of an Au-impregnated bismuth target..... 41
4.2	(Left) HR-TEM image of an isolated Bi nanorod with a diameter of ~10 nm wrapped in a thin Bi ₂ O ₃ sheath. (Right) HR-TEM image of a Bi nanorod showing the excellent ordering of the lattice planes 42
4.3	The corresponding selected area diffraction pattern for the Bi nanorod in Fig. 4.2 42
4.4	Diameter and length distribution of ~100 as-prepared Bi nanorods. The distribution range is broad and the dominant diameters and lengths are ~10 nm and ~200 nm, respectively..... 43
4.5	Proposed growth mechanism for Bi nanorods synthesized via the PLV method 44
4.6	Typical optical path for a FTIR spectrometer where (A) is the source (a Globar lamp), (B) is the interferometer with the fixed and moving mirrors, (C) is the sample position and (D) is the detector..... 46
4.7	FTIR absorption spectrum for ~10 nm Bi nanorods 48
4.8	(Top) Absorption spectra of ~45 nm Bi nanowires grown inside an alumina template. (Bottom) Absorption spectra of ~200 nm thick Bi thin film..... 49

List of Figures (Continued)

Figure	Page
4.9 The absorption spectra reveals the presence of broad absorption bands at 965 cm^{-1} and 1090 cm^{-1} in 200 and 45 nm diameter wires, respectively. The position of these infrared absorption bands have been assigned to an indirect L - T point transition that is not observed in bulk Bi	50
4.10 Dependence of the band gap energy (ΔE) and absorption threshold energy (E_A) on the diameter of Bi nanorods and nanowires. The $\circ$ represent E_A values (right y -axis) reported by Cornelius <i>et al.</i> for their nanowire diameters (top x -axis). The $\blacktriangle$ and $\blacksquare$ data points represent the diameter-dependence (bottom x -axis) for ΔE (left y -axis) reported by Black <i>et al.</i> and this study, respectively. The solid line represents the best fit line showing a $1/d^2$ dependence	54
4.11 Room temperature IR absorption spectra of Bi nanorods annealed in air for 5 hrs. As annealing time increases, the 1393 cm^{-1} peak intensity decreases.....	56
4.12 When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals	57
4.13 UV-visible spectrum of as-prepared Bi nanoparticles with an average diameter of $\sim 6.5\text{ nm}$. A surface plasmon absorption peak is observed at 281 nm	60
4.14 UV-visible absorption spectrum shows the as-prepared Bi nanorods suspended in ethanol. An absorption peak is observed at 302 nm or 4.1 eV	61

CHAPTER 1

INTRODUCTION

A worldwide over-dependence on fossil fuels for energy needs has led to an urgent need for alternative energy and novel energy conversion technologies. Thermoelectric (TE) processes which can convert wasted heat into useful electrical energy (Seebeck effect), [1] or transport the heat away to do refrigeration (Peltier effect) [2] for better power generation devices are mechanisms proving as a plausible solution to our energy needs. These devices have several unique features, such as its all solid-state assembly without movement parts, ease to switch between power generation mode and refrigeration mode, low maintenance cost and ease to couple to other energy conversion devices [3]. This idea of the conversion of wasted heat into electrical power is already finding its way into industry. One of the largest emerging markets is the incorporation of TE power generation for recovery of the large amount of waste heat ($\approx 2/3$ of generated power) from an automobile's exhaust or engine, and harvesting this into usable electrical energy. Meanwhile, TE refrigeration finds its wide application in cooling microelectronics (e.g. central processing unit chips) and optoelectronics (infrared detectors and laser diodes).

The potential of a material for TE applications is determined by the materials' figure of merit, ZT , defined in Eq. 1.1,

$$ZT = \frac{S^2 \sigma T}{\kappa_E + \kappa_L} = \frac{S^2 T}{\rho(\kappa_E + \kappa_L)} \quad (1.1)$$

where S is the Seebeck coefficient, σ the electrical conductivity, ρ the electrical resistivity and κ the total thermal conductivity ($\kappa = \kappa_L + \kappa_E$ the lattice and electronic contributions, respectively). The power factor, $S^2 \sigma T$, (or $S^2 T / \rho$) is usually optimized as a function of carrier concentration (typically around 10^{19} carriers/cm³) [4], through doping in order to attain the largest ZT .

Enhanced TE performance is expected in nano-scaled structures in which the electronic properties can be drastically different from those found in the corresponding bulk material. This direction of nano-scaled research has been motivated by several recent theoretical [5, 6] and experimental investigations [7-9]. Low dimensional materials like ultra-thin films, nanotubes and nanowires can significantly improve the ZT as compared to their bulk counterparts. For example, the theoretical framework for the possible enhancement of ZT in nanowire systems due to quantum confinement effects (QCE) has been discussed in Ref. 5. As one of the dimensions of a bulk material is decreased to a scale that is comparable with the wavelength of the electrons, the motion of the charge carriers (electrons or holes) becomes confined along that direction [10]. Thus, a bulk material begins to exhibit electronic properties that are different from the bulk and can start to exhibit 1D (or 2D) properties if it attains nano-scaled dimension along one (or two) dimensions. This quantum confinement phenomenon leads to a

dramatic change in the electronic density of states (DOS), which will be discussed in further detail later in this chapter.

On the experimental side, recently, Hicks *et al.* [8] showed that PbTe quantum dot structures exhibit a good ZT because of its high carrier mobility and low thermal conductivity. Also, Venkatasubramanian *et al.* [9] showed that $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice materials exhibit a high $ZT \sim 2.5$ at 300 K (Fig. 1.1). By layering these two compounds together, they greatly enhanced the carrier mobility and equally importantly decreased the thermal conductivity. The message is clear: low dimensional structures of TE materials do exhibit higher ZT values than their bulk counterparts (i.e. $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ at 300 K).

Figure 1.1: Temperature dependence of ZT of $10\text{\AA}/50\text{\AA}$ p -type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice compared to those of several recently reported materials [9].

Semimetallic bulk Bi is a poor TE material since the electron and the hole contributions to the thermopower approximately cancel each other [11]. Bi has the smallest effective mass ($\sim 0.001m_o$) of all known materials. The small effective mass of Bi makes it easy to observe QCE. This topic will be discussed in more detail in chapter 2. Bi also has a very long mean free path (~ 0.4 mm at 4 K and ~ 100 nm at 300 K) [12], which makes it a suitable material for studying transport properties. The mean free path is defined as the average distance a particle must travel before colliding with other particles. Lastly, Bi has a low carrier concentration of $\sim 10^{18}$ cm⁻³ which make it favorable material for doping. Such dopants include Te (*n*-type), and Pb or Sn (*p*-type). Bi nanowires with diameters < 50 nm have been predicted to be an excellent TE material based on these unique properties [13]. Bi nanowires are predicted to exhibit a high TE efficiency with an enhanced ZT approaching ~ 2 in small (~ 10 nm) diameter wires (Fig. 1.2). This fact, complied with previously observed QCE in Bi nanowires (dia. ~ 50 nm) prepared by a template-method [14] forms the basis for the research described in this thesis. The overarching goal is to prepare bulk quantities of ~ 10 nm dia. Bi nanorods and confirm QCE through spectroscopy.

Figure 1.2: Predicted ZT of Bi nanowires. As the nanowire diameter decrease, the ZT increases. When diameter reaches ~ 10 nm, the ZT is predicted to be ~ 2 [13].

The easiest way to think about thermoelectricity is to realize that electrical and thermal currents are coupled. The particles that carry electric charge in a material also carry heat. Discussed below are some of the fundamental ideas around how to achieve to best possible TE material, and why nano-structured forms of bulk TE materials warrant further study.

1.1 Figure of Merit

The figure of merit (ZT) is often used for gauging the potential of a particular TE material for realistic applications. As mentioned earlier, ZT is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1.2)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and κ is the total thermal conductivity. Currently, the best TE materials used in devices have a $ZT \approx 1$. The goal for our on going research is to find new materials that can potentially reach a desired $ZT \approx 2-3$. There are, however several hurdles which have to be overcome before higher ZT values can be achieved. As seen through Eq. 1.2, the ZT may be increased by increasing the thermopower and decreasing the electrical conductivity. The ZT may also be increased by increasing the thermal conductivity.

Up to this point in time, the best room temperature TE materials are based on compounds such as Bi_2Te_3 and $\text{Si}_{1-x}\text{Ge}_x$ [15]. Figure 1.3 shows the ZT as a function of temperature for several bulk TE materials. So far, the best known bulk material is $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ which has a $ZT \approx 1$ at 300 K [13].

Figure 1.3: The figure of merit as a function of temperature for a variety of bulk TE materials [15].

1.2 Seebeck Effect

To start this discussion, we will look at the Seebeck coefficient, also known as thermopower. The Seebeck effect was discovered in 1821 by Thomas Seebeck, who found that a voltage existed between two ends of a metal bar when a temperature gradient, ΔT , existed in the bar. The effect is that a voltage is created in the presence of a temperature difference between two different metals or semiconductors. This effect causes a continuous current to flow in the conductors when they form a complete loop. The ΔT across the material leads to an unequal distribution of charge carriers. Let us now

look at a conductor with an applied temperature gradient across it. Free carriers will have more energy at the “hot” end of the material than the “cold” end and electrons (or holes) will thermally diffuse from the hot end (T_H) to the cold end (T_C), carrying their charge with them. As seen in Fig. 1.4, the charge is built up on the cold end and creates

Figure 1.4: Schematic of a conductor showing electrons (or holes) diffusing from the hot end (T_H) to the cold end (T_C).

an electric field inside the sample. When the current generated by this electric field cancels the flow due to the thermal diffusion, equilibrium is reached. The Seebeck coefficient, S , is the ratio between the electric potential (ΔV) and the temperature gradient (ΔT) between the ends of the sample as seen in Eq. 1.3, giving the Seebeck coefficient units of (V/K). The sign of Eq. 1.3 is determined by the charge build up at the cold end, whether it is positive or negative. Measuring the Seebeck coefficient is one way to determine whether the dominant charge carriers are electrons or holes. Figure 1.5 shows a schematic of a typical TE device. The Seebeck effect is the basis for many TE power

$$S = \frac{\Delta V}{\Delta T} \quad (1.3)$$

generation devices. In the power generation mode, in which the Seebeck effect is used, heat is applied to one side of the device and as a result, a voltage develops across the n and p legs that can be used to convert part of the heat into electrical power. Knowing that the Seebeck coefficient is a function of temperature allows us to calculate the Peltier coefficient.

Figure 1.5: Schematic of a TE couple made of an n -type and p -type semiconductor material. A temperature gradient is applied across the device and a direct conversion of heat into electrical power is achieved [15].

1.3 Peltier Effect

A very similar effect to the Seebeck effect is the Peltier effect. This effect was observed in 1834 by Jean Peltier. The Peltier effect is the reversible exchange of heat from a junction of dissimilar materials in the presence of a current passing through the junction, which is held at a constant temperature. The Peltier coefficient, Π , is the ratio of the rate of heating (or cooling) to the electrical current passing through the junction and can be defined as

$$\Pi = \frac{1}{I} \frac{dQ}{dt} \quad (1.4)$$

where I is the current and $\frac{dQ}{dt}$ is the heat flow per unit of time. Due to this effect, heat is generated (or absorbed) at the junction of the two materials. Figure 1.6 shows a schematic of this phenomenon. Imagine that on the bottom is a material of type A and the one on the top is a material of type B. Both of the materials will be carrying heat towards the junction and thus, some power will be produced.

Figure 1.6: Schematic of the Peltier effect showing a current flowing through two different materials. At the junction, heat is produced which can be used as energy.

The Peltier effect is the basis for many TE refrigeration devices [16]. Figure 1.7 below illustrates a typical Peltier effect device. Heat is generated by passing a current through the two materials, thus creating a temperature gradient and heat is absorbed on the cold side and flows through the material and is rejected on the other side. Thus, a refrigeration device is born. Please note that power generation (Seebeck effect) and refrigeration (Peltier effect) are actually equivalent to each other, and they are reversible.

Figure 1.7: Schematic of a TE couple made of an n -type and p -type semiconductor material. A current is passed through the two materials, heat is absorbed and then rejected as cool air [15].

1.4 Thomson Effect

The last of the thermoelectric effects is the Thomson effect. Let us consider a material with a current flowing through it and a temperature gradient that is applied to it (see Fig. 1.8). Due to the ΔT , thermal energy is generated all the length of the material. This idea is very similar to the Peltier effect and thus it can be thought of as a series of many small Peltier junctions, each of which generates heat. If the temperature difference is small enough, $q = \frac{\Pi}{\Delta T}$, where Π is the Peltier effect [3].

Figure 1.8: Schematic of the Thomson effect. A current flows through the material and a temperature gradient is applied to it, thus thermal energy is created.

1.5 Density of States

There are several theories which suggest enhanced TE properties in low dimensional systems. As the characterization length of the material is decreased with relation to the wavelength of the electrons, the motion of the electrons (or holes) is confined in one direction, leading to a change in the shape of the electronic density of states (DOS). Figure 1.9 shows the DOS as a function of the energy for a 3D bulk material, 2D quantum well, 1D quantum wire and 0D quantum dot.

Figure 1.9: Electronic density of states for 3D bulk materials, 2D quantum well, 1D quantum wire and 0D quantum dot [17].

The parabolic shape of the DOS for bulk materials implies that the electron density surrounding the Fermi level is small. The spike-like shape of the DOS for quantum wires implies that the electronic states are enhanced near the Fermi level, thus resulting in an increased thermal power factor $S^2 \sigma$. Dresselhaus *et al.* [13] proposed that: (i) the Seebeck coefficient being directly related to the slope of the DOS at the Fermi surface (Eq. 1.5) and (ii) boundary scattering at the interface reduces the thermal conductivity much more than the electronic conductivity can lead to superior TE properties in nanostructured materials.

$$S = \frac{\pi^2 k^2 T}{3e} \left. \frac{\partial \ln \sigma}{\partial E} \right|_{E=E_F} \quad (1.5)$$

Equation 1.5 is commonly referred to as the Mott relation [18] where k is the Boltzmann constant, T is the temperature, e is the electrical charge of an electron, σ is the electrical conductivity and E is the energy of the charge carriers.

In the next chapter, the foundation for this thesis is laid out through discussion of QCE and enhanced properties of Bi nanorods prepared by the template-method.

CHAPTER 2

BACKGROUND AND THEORY

Bismuth, in bulk form, is a semimetal with a rhombohedral crystal structure. Figure 2.1(a) shows an image of the crystal structure with 4 unit cells (blue dashed lines). Figure 2.1(b) shows the hexagonal crystal pattern created by the trigonal symmetry.

Bismuth has a small band gap overlap (~ 38 meV) between the conduction band at the L -points and the valence band at the T -point in the Brillouin zone [12]. The location of the electron (L -point) and hole (T -point) carrier pockets in the Brillouin zone [14] of Bi is shown in Fig. 2.2. A very interesting feature about Bi is its highly anisotropic Fermi surface and non-parabolic L -point energy bands.

The Fermi energy can be defined as

$$E_F = -\alpha(T)kT \quad (2.1)$$

where $\alpha(T)$ specifies the number of particles in a particular system at a certain temperature, T , and k is the Boltzmann's constant [19].

At low temperature (77 K) the electronic band structure of bulk Bi at the L -points reveals highly non-parabolic electronic energy bands. These bands are mirror images of each other and are separated by a small energy gap, $E_{gL} = 13.6$ meV. [20]. Figure 2.3 shows a schematic diagram of the Bi band structure at the L -points and T -point near the

Fermi energy level, showing the band overlap, $\Delta_0 = 38$ meV, of the L -point conduction band and the T -point valence band.

Figure 2.1: (a) Bismuth crystal structure showing 4 unit cells. Z-axis is pointing upward. (b) Hexagonal pattern created by the trigonal symmetry of Bi. Z-axis is pointing out of the page.

Figure 2.2: The Brillouin zone of Bismuth [14].

Figure 2.3: Schematic diagram of the Bi band structure at the L -points and T -point near the Fermi energy level, showing the band overlap, E_0 , of the L -point conduction band and the T -point valence band. The L -point electrons are separated from the L -point holes by a small band gap E_{gL} . At $T = 77$ K, $\Delta_0 = 38$ meV and $E_{gL} = 13.6$ meV [20].

2.1 Semimetal-to-Semiconductor Transition

The small band overlap, with tiny ellipses of electrons at the L -point and of holes at the T -point, is predicted to change to a small indirect band gap (ΔE) when the diameter of Bi nanowires decreases below 50 nm [21, 22]. This indirect energy band gap can be measured experimentally in the mid-infrared spectral regime. This ΔE can be observed as an absorption band using infrared spectroscopy and may be tracked as a function of wire diameter, d . In smaller diameter nanowires, the ellipses at the L and T -points split into sub-bands causing an increase in the energy gap and is related to the nanowires diameter d by,

$$\Delta E \approx \frac{\hbar^2 \pi^2}{m^* d^2} \quad (2.2)$$

where m^* is the electron effective mass ($0.001m_o$ - $0.26m_o$, depending on the crystalline direction) [12] and $\hbar$ is the Planck's constant. Cornelius *et al.* [20] have observed this $1/d^2$ dependence in their infrared absorption threshold data obtained from individual Bi nanowires with diameters between 400 and 30 nm. They ascribed the blue-shift of the absorption threshold (E_A) with decreasing d , to the d -dependent splitting of the valence and conduction bands (discussed later in this thesis), and consequently to the resulting energy gaps. In their study, the d -dependent absorption threshold was evident from their plots of $A(\omega)$ vs. ω , where $A(\omega) \approx 1 - T(\omega)$, ω ranged between $800 - 5500 \text{ cm}^{-1}$, and $T(\omega)$ is the infrared transmission spectrum for each nanowire. Black *et al.* [14, 23] studied the behavior of similar Bi nanowires although with a predominantly $\langle 012 \rangle$ orientation rather than the predominantly $\langle 110 \rangle$ orientation of Cornelius *et al.* Hence, for a small enough diameter wire, the lowest conduction sub-band will no longer overlap with the highest valence sub-band in energy, thus making the nanowire semiconducting [24, 25]. This transition is shown schematically in Fig. 2.4 and is known as a semimetal-to-semiconductor transition. The diameter at which this transition takes place is called the critical diameter. Figure 2.5 shows the highest valence sub-band energy and the lowest conduction sub-band energy plotted as a function of the nanowire diameter along the trigonal direction, $\langle 012 \rangle$, for a Bi nanowire at 77 K [5]. As seen from the figure, the critical wire diameter is calculated to be 54.2 nm. This is where the lowest conduction

sub-band edge formed by the L -point electrons crosses the highest T -point valence sub-band edge and a semimetal-to-semiconductor transition occurs.

Figure 2.4: Schematic diagram of the energy bands in a Bi nanowire undergoing a semimetal-to-semiconductor transition. The lowest conduction sub-band (L -point) moves up in energy and the highest valence sub-band (T -point) moves down in energy [24, 25].

Figure 2.5: Calculation of the lowest T -point and highest L -point sub-band energies as a function of wire diameter at 77 K [5].

Several groups have confirmed this transition in Bi nanowires through measurements of temperature and magnetic field dependencies of the electrical resistance [6, 26] and room temperature infrared absorption spectroscopy [14, 20, 23]. Recently, Wang *et al.* [27] have also confirmed the semimetal to semiconducting transition in 5-500 nm diameter Bi nanoparticles prepared by reducing Bi^{3+} with sodium borohydride in the presence of poly(vinylpyrrolidone). However, Huber *et al.* [28] recently reported the lack of semiconducting nature in their 30 nm diameter Bi nanowires and have interpreted their experimental results in terms of surface-induced charge carriers in a spherical Fermi surface pocket.

2.2 Quantum Confinement

Low dimensional materials continue to attract much interest due to their promising potential use for applications in the future. The potential advantages of these materials arise due to spatial confinement of the carrier charges and corresponding modification of their DOS [24]. In recent years, Bi has been the focus of quantum wires for this purpose of modifying its DOS at lower dimensions [29]. Due to their semimetal-to-semiconducting transition, Bi nanowires have been suggested to be good TE materials [30]. This prediction is likely due to some of their unique properties, such as their long mean free path and high carrier concentrations. QCE can be experimentally quantified through fourier-transform infrared (FTIR) and UV-visible (UV-vis) spectroscopy.

This effect can be seen by looking at the work by Hu *et al* [31] which examines the band gap of ZnO nanoparticles, where they calculated the average particle size of the nanoparticles, using the effective mass model [32]. The equation for the band gap energy (E_g) in ZnO nanoparticles, using this model, can be expressed as

$$E_g = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2er^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e}{4\pi\epsilon\epsilon_0 r} - \frac{0.124e^3}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1} \quad (2.3)$$

where E_g^{bulk} is the bulk band energy, $\hbar$ is Plank's constant, r is the particle radius, m_e^* is the electron effective mass, m_h is the hole effective mass, m_o is the free electron mass, e is the charge on the electron, ϵ is the relative permittivity, and ϵ_0 is the permittivity of free

space. Figure 2.6 shows a plot of the calculated energy gap versus particle size using the effective mass model for ZnO nanoparticles [31, 33]. Using this model, it can be calculated that no band gap energy changes will be seen until the particle size is reduced to ~ 4 nm and below. This is due to the fact that ZnO, like Bi, has a relatively small effective masses ($m_e = 0.26m_o$ and $m_h = 0.59m_o$) [34].

Figure 2.6: Calculated band gap energy versus radius for ZnO nanoparticles based on the effective mass model [31].

The above calculation is for a 0D quantum dot. What happens when the 1D quantum wire system is studied? Gudiksen *et al.* [35] recently explored these size-dependent effects on the photo-luminescence in InP nanowires. The effective mass model was modified by using radially symmetric wave functions for both electrons and

holes. The calculated energy shift, relative to the bulk band gap, can be expressed as a function of the nanowire radius, R . This new wave function can be written as

$$\Delta E = \frac{\hbar^2}{2m^*} \left(\left(\frac{\alpha_{01}}{R} \right)^2 + \left(\frac{\pi}{L} \right)^2 \right) - \left\langle \Psi(x_e) \Psi(x_h) \left| \frac{e^2}{\varepsilon |x_e - x_h|} \right| \Psi(x_h) \Psi(x_e) \right\rangle \quad (2.4)$$

where m^* is the reduced effective exciton mass ($m_e m_h / (m_e + m_h)$), ε is the dielectric constant of InP, L is the length of the cylinder, and α_{01} is the first zero of the zeroth-order Bessel function (2.405) [36]. The first term of the above equation is dependent on the sum of the inverse radius and length of the nanowire. The second term is the attractive Coulomb interaction between the electron and the hole. As seen from the above expression, the only term which strongly influences the band gap energy is the inverse sum of the first term.

It has already been discussed in Fig. 2.5 that Bi exhibits a semimetal-to-semiconducting transition at ~ 54 nm. The above equation (Eq. 2.4) can tell us at what critical value d , the Bi nanorods will exhibit QCE. Figure 2.7 shows the predicted band gap energy versus the nanorods diameter using the modified effective mass model for Bi nanorods. For Bi nanorods, the following conditions were applied to Eq. 2.4.

Figure 2.7: Plot of the predicted band gap energy as a function of nanorod diameter based on the modified effective mass model for Bi nanorods.

The electron effective mass, m_e , is $0.001m_o$, m_h is $0.059m_o$, ε is ~ 100 and the bulk band gap, E_g^{bulk} is 38 meV. As can be seen from the above graph, like ZnO nanoparticles, Bi nanorods are not predicted to show any QCE until a nanorod diameter of ~ 35 nm is reached.

In the following chapter, we will first discuss the state-of-the-art synthesis of Bi nanowires. Next, we will discuss details of a pulsed laser vaporization (PLV) technique that was previously developed for synthesis of carbon nanotubes, and how our PLV technique can help us prepare ~ 10 nm Bi nanorods in bulk quantities.

CHAPTER 3

SYNTHESIS TECHNIQUES

During the past decade, semiconductor nanomaterials, especially nanowires, have received great attention as potential “new” materials for the thermoelectric and electronics fields. Semiconducting nanomaterials such as Si [37], Ge [38], Bi₂Te₃ [39], Si_{1-x}Ge_x [40] and PbTe [39] have been synthesized a variety of ways, each of which has its own advantages and disadvantages. Some of the methods, such as the template-assisted and physical evaporation methods are an excellent way of synthesizing materials, but are not good at synthesizing large quantities of TE nanomaterials. However, other methods, such as chemical vapor deposition and hydrothermal growth methods are great sources for preparing large quantities of nanostructured materials. Discussed below are some of these methods for synthesizing TE nanomaterials.

3.1 Template-Based Synthesis

The template-based method is conventionally known as the “brute-force” method for synthesizing 1D nanomaterials. In this technique, the template (usually anodic alumina with pre-formed nano-sized channels) serves as a membrane by which other materials with similar morphologies can be synthesized, see Fig. 3.1. The materials generated through such a membrane attain the shape that is similar to that of the channels

in the membrane. The nanoscale pores are usually filled by the material (in its molten state) and then pressure-injected into the alumina template. The nanowires are produced after the pressure-injected material solidifies in the nano-size channels and the template is dissolved [41]. An anodic alumina template consisting of a hexagonally packed 2D array of cylindrical pores with a uniform size has been used for preparing Bi nanowires [14]. The size of the pores can be varied to obtain different sized nanowires. Figure 3.2 shows the scanning electron microscopy images of the template before after molten Bi was injected. However, there are some drawbacks to this method. It is difficult to obtain highly crystalline forms of 1D structures, and this method can be time consuming because of the various steps involved in the synthesis process.

Figure 3.1: 3D representation of the alumina template method.

Figure 3.2: Left: SEM image of the porous alumina anodic layer with ~ 40 nm pore diameter. Right: SEM image of Bi nanowire array after the template has been filled with Bi.

3.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) synthesis is probably one of the most widely used methods for the synthesis of carbon nanotubes. However, in recent years, CVD has become the popular synthesis method for semiconducting nanostructures. It is the most desirable method due to its ability to produce nanostructured materials in bulk quantities.

Figure 3.3 shows a schematic of a typical CVD setup which consists of heated quartz (or ceramic) tube reactor that is closed on both ends to prevent undesirable oxidation of the materials. Substrates are placed inside the reactor and are heated to a desired temperature in the presence of a carrier gas (usually Ar gas). Once the reactor temperature is stabilized, the reactants or chemicals are introduced into the reactor. As the name suggests, desired products are obtained through modification of the reactants in their vapor state. The products are collected on the substrates and can be harvested after

the reactor cools down to room-temperature. As mentioned before, CVD is most notably used for synthesizing carbon nanotubes, but recently it has been used in the production of semiconducting and nano-structured TE materials such as PbTe [42] and Bi₂Te₃ [43]. For example, Ge nanowires [44] synthesized by this method are shown in Fig. 3.4.

Figure 3.3: Schematic of the CVD method used to prepare a variety of nanomaterials.

Figure 3.4: SEM image of Germanium nanowires synthesized by CVD [44].

3.3 Hydrothermal Method

Materials, such as III-V and II-VI group semiconductors, carbides, nitrides and phosphides, are traditionally prepared by solid state or gas-phase reactions. They have been mostly prepared using precursors and the products may be amorphous or poorly crystalline and thus a crystallization treatment at higher temperatures is necessary [45].

Hydrothermal synthesis is one of the important methods used for producing nanomaterials. A hydrothermal system is usually maintained at a temperature beyond 100 °C and the inner pressure of the water exceeds the ambient pressure (Fig. 3.5). This is favorable for the crystallization of the nanomaterials. Most notably, Groshens *et al.* [46] describes a low temperature approach to Bi_2Te_3 by means of eliminating the reaction conducted in hexane at -30 °C. Then, Ritter *et al.* [47] reported a room temperature

process of co-precipitation of Bi_2Te_3 precursor in an aqueous solution. This method is similar to the hydrothermal synthesis method, but is known as the solvothermal process. The solvothermal process takes place in a non-aqueous solvent which is sealed in an autoclave and maintained in its superheated state. This is necessary to keep the reactants and products from oxidation. The crystal growth takes place in an autoclave with a temperature gradient that is maintained at each end. This is so the hotter end dissolves the crystals and the cooler end seeds the growth.

Figure 3.5: Schematic of the hydrothermal/solvothermal method used for producing nanomaterials.

3.4 Thermal Evaporation

Thermal evaporation is perhaps the most common and versatile synthesis method used today which produces nanomaterials in limited quantities. Recently, Z.L Wang *et al.* [48] grew ZnO nanowires using thermal evaporation. Their synthesis is based on the use of oxide powders without the presence of a catalyst. Finely ground ZnO powder was placed in an alumina boat and placed in the center of a quartz tube. Substrates were positioned at the end of the tube to collect the as-synthesized material. The setup is almost identical to that of the CVD method, where the temperature, pressure and evaporation time are all controlled. The reaction takes place with the presence of Ar. Figure 3.6 shows the as-synthesized ZnO material under transmission electron microscopy.

Figure 3.6: TEM image of the as-synthesized ZnO nanobelts by thermal evaporation [48].

3.5 Pulsed Laser Vaporization

Pulsed laser vaporization (PLV) was one of the first methods developed for synthesizing nanowires. Morales *et al.* [37] at Harvard University first used the principle of the vapor-liquid-solid growth process, to be explained in detail later, in their PLV apparatus to grow small diameter Si and Ge nanowires. This method is the method used in our synthesis of Bi nanorods. Figure 3.7 shows a schematic of our PLV system.

Figure 3.7: Schematic representation of our pulsed laser vaporization setup.

In our PLV method, a Nd:YAG laser (Yttrium-aluminum-garnet, 1064 nm excitation, 650 mJ/pulse, 10 Hz) is used to ablate a rotating target with the elemental composition desired in the nanowire forms. For example, for preparing Bi nanowires or nanorods, the target is prepared from Bi powder (Alfa Aesar, 99.5%) which contains one

atomic percent Au catalyst (Alfa Aesar, 99.96%). The target is placed on a rotating rod which resides inside a quartz tube reactor which was maintained at ~ 200 °C. The quartz tube is sealed at both ends and a continuous flow of argon (flow rate ~ 150 sccm) and hydrogen (flow rate ~ 15 sccm) assists in carrying the ablated material downstream to the water-cooled copper cold finger is placed inside the quartz tube. As the target is ablated, the vaporized material and catalyst particles flow downstream and condense on the cold finger [49]. During the reaction, the catalyst particles serve as the seed for the nanowire growth. After the reaction, the reactor is cooled to room temperature and the ablated material is collected from the cold finger. Figure 3.8 shows a TEM image of Si nanowires produced via the PLV by Morales *et al* [37]. As seen in the figure, a Fe catalyst particle (indicated by the arrows) is present at the tip of the nanowires.

The PLV process described above is extremely versatile and can be used for synthesizing a wide range of different nanowires. PLV also has another unique feature. By varying the composition of the material in the target, one can synthesize nanowires with different stoichiometric compositions. This variation can be used to tailor the electronic and optical properties of nanostructured materials. Another advantage to the PLV method is that one can control the diameter of the nanowires by controlling the diameter of the catalyst particle used in the experiment.

Another similar PLV process is one in which substrates are coated with the catalyst particles and placed downstream from the target inside the reactor. In this approach, the catalyst particles are placed on the substrates rather than implanting them in

the target. The ablated material is transformed into nanostructures on the substrates (rather than the cold finger) since the substrates contain the catalyst particles.

Figure 3.8: TEM image of Si nanowires produced by the PLV method from the $\text{Si}_{0.9}\text{Fe}_{0.1}$ target. The material was collected from the cold finger and the arrows indicate the catalyst particle [37].

3.6 Growth Mechanisms

An interesting aspect of 1D structures is the growth mechanism responsible for transformation of the material from the bulk form to the 1D form [50]. The growth of nanowires via a gas phase reaction involving the vapor-liquid-solid (VLS) process has been widely studied. In the 1960s, Wagner and Ellis [51] proposed a mechanism for the growth of micro-sized Si whisker in the presence of Au particles. According to this mechanism, the anisotropic crystal growth is promoted by the presence of the liquid

alloy/solid interface. As the liquid droplet becomes supersaturated with the vapor reactant, whisker growth will occur by means of a precipitation process of the reactant. This mechanism has been widely accepted and applied for understanding the growth of various nanowires including Si and Ge [37]. A schematic of this VLS growth process is shown in Fig. 3.9, where (A) a laser beam ablates the target containing Si and Fe catalyst. (B) The dense vapor condenses into small clusters of molten Si and Fe particles. (C) The liquid becomes Si/Fe nanoclusters supersaturated with the Si reactant and nanowire growth begins. (D) The growth of the nanowires ends as it is cooled to room temperature and the Fe catalyst remains at the tip of the Si nanowire.

Figure 3.9: Proposed VLS growth mechanism for Si nanowires [37].

Since the catalyst particle templates the growth, the diameter of the nanowires is dictated by the diameter of the catalyst particle. The PLV and thermal evaporation methods provide an efficient means to obtain uniform-sized nanowires by controlling the

catalyst particle size placed on the substrates. For example, Gudiksen *et al.* [52] proved this point in their research involving GaP nanowires by varying the size of the gold catalyst particles. With the knowledge of the phase diagram of the reacting species, the growth temperature can be set at the eutectic point of the material. For example, Duan *et al.* [53] describes

Figure 3.10: Pseudo-binary phase diagram for GaAs and Au. The liquid Au-Ga-As component is represented as L [54].

the synthesis of GaAs nanowires by PLV using gold particles as the catalyst. From the binary phase diagram of Au-GaAs, the appropriate composition of Au versus GaAs can be identified. This information can then be used to make appropriate targets for PLV. The phase diagram, shown in Fig. 3.10, shows that Au-Ga-As liquid and GaAs solid are

the principle phases above 630 °C in the GaAs rich region. This implies that Au can indeed serve as a catalyst in the growth of the nanowires.

From the knowledge of the phase diagram for Bi [55], as seen in Fig. 3.11, we were able to find the right temperature for the synthesis with 1 atomic percent Au and 99 atomic percent Bi. The diagram shows that Au-Bi liquid is the principle phase above 271 °C in the Bi rich region, thus Au may be used to catalysts Bi.

Figure 3.11: Binary phase diagram for Bi and Au [55].

CHAPTER 4

EXPERIMENTAL METHODS, RESULTS AND DISCUSSION

4.1 Electron Microscopy

The morphology of the as-prepared nanomaterials obtained from a PLV of a Au-impregnated Bi target was analyzed via high resolution transmission electron microscopy (HR-TEM). The TEM images were collected using a Hitachi 9500 microscope which operates at 300 kV. The imaging was performed in the bright field of the microscope. Samples for the TEM analyses were prepared by taking the as-prepared material (from the cold finger) and dispersing them in ethanol, followed by sonication for ~30 sec. or until a uniform solution was obtained. Next, 1-2 drops of the solution were deposited on a 200 mesh Holey Carbon TEM Cu grid for analysis. In addition to TEM, the crystal structure of the 1D structures was determined by using electron diffraction. Electron diffraction analysis was performed using a small selected area aperture (SAD mode) on a selected area of the 1D structures.

Figure 4.1 shows a transmission electron microscope image of the as-produced deposit collected on the cold finger. The deposit predominantly contains filamentous nanostructures which are dispersed amongst spherical Bi nanoparticles and flat Bi₂O₃ sheets. When viewed under a

Figure 4.1: TEM image of the as-prepared Bi deposit obtained from a pulsed laser vaporization of an Au-impregnated bismuth target.

HR-TEM, the filamentous objects resemble nanorods (short 1D structures) as opposed to nanowires. The nanorods contain a crystalline core of Bi encapsulated in a thin (< 2 nm) Bi_2O_3 layer (Fig. 4.2). From the analysis of the sharp SAD pattern (Fig. 4.3), the nanorod growth direction was found to be $\langle 012 \rangle$. Furthermore, the lattice spacing of the planes oriented along the length of the Bi nanorods was found to be 0.328 nm, which is consistent with the $\langle 012 \rangle$ growth direction in the trigonal Bi crystal structure. The length and diameter distributions for ~ 100 nanorods are plotted in Fig. 4.4. The dominant nanorod diameter is ~ 10 nm with an average length of ~ 200 nm.

Figure 4.2: (Left) HR-TEM image of an isolated Bi nanorod with a diameter of ~ 10 nm wrapped in a thin Bi_2O_3 sheath. (Right) HR-TEM image of a Bi nanorod showing the excellent ordering of the lattice planes.

Figure 4.3: The corresponding selected area diffraction pattern for the Bi nanorod in Fig. 4.2.

Figure 4.4: Diameter and length distribution of ~100 as-prepared Bi nanorods. The distribution range is broad and the dominant diameters and lengths are ~10 nm and ~200 nm, respectively.

The PLV technique has been used by several groups [37] for preparing 1D structures of various elemental compositions. The favored growth mechanism for these 1D structures is the VLS mechanism in which a liquid metal cluster (or catalyst) acts as the energetically favored site for absorption of gas-phase reactants. Upon supersaturation of the liquid metal cluster, 1D structures are formed and the catalyst particle typically resides at one end of the 1D structure. While it is reasonable to expect our Bi nanorods to be catalyzed via the VLS mechanism, we do not find evidence from our electron microscopic studies for the presence of the gold catalyst particles in the nanorods (as can be seen from Fig. 4.2). These finding suggests that a novel growth mechanism may be involved. One plausible explanation for the absence of Au catalyst particles in our Bi nanorods is provided in Fig. 4.5. (A) Laser ablation of the target creates a vapor of Bi and Au. (B) The hot vapor condenses into small molten particles as the Bi and Au

start to cool through collisions with the buffer gas. (C) Nanorod growth begins after the liquid becomes saturated with Bi and will continue to grow while the Bi-Au nanoclusters remain in a molten state. (D) As the nanorods move through the cooler region of the quartz tube furnace, the Au catalyst solidifies and cannot sustain catalytic growth of the wires any further. (E) While the Au has solidified, the Bi is still in a somewhat molten state and expels the Au catalyst and wire growth subsequently terminates.

Figure 4.5: Proposed growth mechanism for Bi nanorods synthesized via the PLV method.

4.2 FTIR Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a vibrational spectroscopy technique. Absorption in the infrared region results in vibrational and rotational excitations of the molecules and the absorption frequency depends on the vibrational frequency of the molecules. However, the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule, and thus

depends on the change in the dipole moment that occurs as a result of molecular vibration [56]. Due to this, a molecule will absorb infrared light only if the absorption causes a change in the dipole moment. Most compounds except for elemental diatomic gases such as H_2 and O_2 all have infrared active spectra and can yield a wavelength dependent spectra [57].

In a FTIR instrument, the monochromator and the slits are replaced by an interferometer. In the interferometer, the light passes through a beamsplitter, which sends the light in two different directions at right angles from each other. One beam goes to a stationary mirror then back to the beamsplitter. The other goes to a moving mirror. The motion of the mirror makes the total path length variable versus that taken by the stationary mirror beam. When the two beams meet up again at the beamsplitter, they recombine, but the difference in path lengths creates constructive and destructive interferences, known as an interferogram. Figure 4.6 shows the typical beam path in a FTIR spectrometer.

The recombined beam passes through the sample and the sample absorbs at different wavelengths characteristic of its spectrum. It then subtracts specific

Figure 4.6: Typical optical path for a FTIR spectrometer where (A) is the source (a Globar lamp), (B) is the interferometer with the fixed and moving mirrors, (C) is the sample position and (D) is the detector.

wavelengths from the interferogram and the detector reports variations in intensity versus time for all wavelengths simultaneously.

If one thinks about it, intensity versus time is an odd way to record a spectrum. A function called a Fourier transform allows one to convert intensity versus time spectrum into an intensity versus frequency spectrum. This is possible because time and frequency are reciprocals of one another as can be seen by Eq. 4.1

$$A(r) = \sum X(k) \exp\left(-2\pi \frac{irk}{N}\right) \quad (4.1)$$

where $A(r)$ and $X(k)$ are the frequency domain and time domain points, respectively, for a spectrum of N points [56].

A transmittance spectrum can also be obtained from FTIR spectroscopy. The absorbance spectrum can be calculated from the transmittance spectrum using the Eq. 4.2 below [58].

$$A = -\log_{10} T \quad (4.2)$$

Where A is the absorbance and T is the transmittance.

A Bruker FTIR spectrometer (model IFS 66v/s) equipped with a deuterated triglycine sulfate detector was used to collect the infrared absorption spectrum of the as-prepared Bi nanorods in the range of $400 - 4000 \text{ cm}^{-1}$. A potassium bromide (KBr) beamsplitter was used in the interferometer. About ~ 3 mg of the as-prepared deposit was mixed with ~ 50 mg of KBr powder and pressed into a 5 mm diameter pellet. The sample chamber was evacuated down to 0.002 mbar in order to eliminate the interfering infrared (IR) absorption by the water vapor and CO_2 present in the ambient atmosphere. Figure 4.7 shows the room temperature IR spectra for our 1D Bi nanorods.

Recently, Black *et al.* [14] measured their ~ 45 nm Bi nanowires grown inside an alumina template. Figure 4.8 shows the corresponding absorption spectra of the free standing Bi nanowires grown via the alumina template method and a spectrum which corresponds to that of a thin film of Bi. The Bi thin film was ~ 200 nm thick and could be

thought of as bulk Bi. The peak seen at $\sim 1090\text{ cm}^{-1}$ has been ascribed to the indirect transition between the L -point and the T -point.

Figure 4.7: FTIR absorption spectrum for $\sim 10\text{ nm}$ Bi nanorods [59].

Figure 4.8: (Top) Absorption spectra of ~ 45 nm Bi nanowires grown inside an alumina template. (Bottom) Absorption spectra of ~ 200 nm thick Bi thin film [14].

Figure 4.9 shows the previously reported infrared absorption band at ~ 965 cm^{-1} for 200 nm diameter nanowires [23]. This band is found to be blue-shifted in energy to ~ 1090 cm^{-1} in the infrared spectrum for a 45 nm diameter Bi nanowires [23]. Interestingly, a further blue-shift in energy to ~ 1393 cm^{-1} is observed for our ~ 10 nm Bi nanorods, and the infrared band is clearly resolved into two main absorption peaks centered around 1393 cm^{-1} and 1460 cm^{-1} (Fig. 4.7). An additional third absorption peak manifests as a weak shoulder at 1355 cm^{-1} .

In an independent infrared experiment, we have confirmed that the infrared band featured in Fig. 4.7 is not due to the presence of the residual Bi_2O_3 present in the as-obtained deposit.

Figure 4.9: The absorption spectra reveals the presence of broad absorption bands at 965 cm^{-1} and 1090 cm^{-1} in 200 and 45 nm diameter wires, respectively. The position of these infrared absorption bands have been assigned to an indirect L - T point transition that is not observed in bulk Bi [23].

It is known that Bi_2O_3 has very little optical absorption in the spectral range depicted in Fig. 4.7 [14]. Under identical synthesis conditions used in this study, the PLV of a rotating Bi target without the gold catalyst yields a cold-finger deposit which does not contain the nanorods, and the 1393 cm^{-1} feature is absent in its infrared spectrum.

Interestingly, we can estimate the mass of the electron from the 1393 cm^{-1} absorption peak by rewriting Eq. 2.2. as,

$$\Delta E = \frac{\pi^2 \hbar^2}{m' m_o d^2} \quad (4.3)$$

$$m' = \frac{\pi^2 \hbar^2}{m_o d^2 \Delta E} \quad (4.4)$$

where m' is effective mass component and m_e is the free electron mass. We obtain an effective mass component of $0.0433m_o$ which compares favorably with the values reported in Table 4.1 by Lin *et al.* [5]. This values correspond to the components along the [01-12] direction and wire axis ($m_{z'}$) at the electron pockets $L(B)$ and $L(C)$ [See Fig. 2.2 for more details].

Mass component		Trigonal	Binary	Bisectrix	$[01\bar{1}2]$	$[10\bar{1}1]$
e^- pocket $L(A)$	$m_{x'}$	0.1175	0.0023	0.0023	0.0029	0.0024
	$m_{y'}$	0.0012	0.2659	0.0012	0.0012	0.0012
	$m_{z'}$	0.0052	0.0012	0.2630	0.2094	0.2542
e^- pocket $L(B)$	$m_{x'}$	0.1175	0.0023	0.0023	0.0016	0.0019
	$m_{y'}$	0.0012	0.0016	0.0048	0.0125	0.0071
	$m_{z'}$	0.0052	0.1975	0.0666	0.0352	0.0526
e^- pocket $L(C)$	$m_{x'}$	0.1175	0.0023	0.0023	0.0016	0.0019
	$m_{y'}$	0.0012	0.0016	0.0048	0.0125	0.0071
	$m_{z'}$	0.0052	0.1975	0.0666	0.0352	0.0526
T -point hole pocket	$m_{x'}$	0.0590	0.6340	0.6340	0.1593	0.3261
	$m_{y'}$	0.0590	0.0590	0.0590	0.0590	0.0590
	$m_{z'}$	0.6340	0.0590	0.0590	0.2349	0.1147

Table 4.1: Calculated effective mass components of each carrier pocket for determining the band structure in Bi nanowires at 77 K along the indicated crystallographic directions, based on the effective mass parameters of bulk Bi [12, 60]. The z' direction is chosen along the wire axis and all mass values are in units of the free electron mass, m_o [23].

Figure 4.10 shows a plot of ΔE vs. d for nanowires studied by Black *et al.* [23] and our ~ 10 nm diameter nanorods, and the d -dependence for the absorption threshold E_A reported by Cornelius *et al* [20]. As seen from Fig. 4.10, the frequency shift is consistent with a $1/d^2$ behavior as predicted by quantum confinement. Similarly, Wang *et al.* [61] uncovered a $1/d^2$ dependence for the volume plasmon excitation of Bi nanoparticles investigated by electron energy loss spectroscopy.

It should be mentioned that the splitting we see in our infrared absorption band does not seem to arise directly from the diameter distribution of Bi nanorods present in our samples. If we suppose that the energies of the bands are inversely proportional to the square of the diameter of the nanorods (cf. Eq. 2.2), and that the center absorption line

comes from the 10 nm diameter nanorods (with about 30 planes of atoms), then the smallest energy splitting would be

$$\approx \Delta E [1 - (30/31)^2] = (1393 \text{ cm}^{-1}) (0.06348) = 88 \text{ cm}^{-1}$$

which is much larger than we see. In addition, there would be multiple absorption bands, spread out over perhaps 2000 cm^{-1} .

What is the origin of these absorption bands? There is evidence for and against a semimetal to semiconductor transition as the diameter of the Bi single crystal nanowires or nanorods decrease. The MIT group [14, 23], for example, show calculations that indicate that the bulk (not including surface states) electronic structure will show such a transition at ~ 50 nm in square and circular cross-section nanowires. They are able to interpret the absorption spectra that they obtain in 45 nm Bi nanowires in terms of inter-subband transitions [14] or an interband indirect transition in the calculated electronic structure of their wires.

Figure 4.10: Dependence of the band gap energy (ΔE) and absorption threshold energy (E_A) on the diameter of Bi nanorods and nanowires. The $\circ$ represent E_A values (right y-axis) reported by Cornelius *et al.* [20] for their nanowire diameters (top x-axis). The $\blacktriangle$ and $\blacksquare$ data points represent the diameter-dependence (bottom x-axis) for ΔE (left y-axis) reported by Black *et al.* [23] and this study, respectively. The solid line represents the best fit line showing a $1/d^2$ dependence [59].

On the other hand, Huber *et al.* [28] found that the resistive Shubnikov-de Haas (SdH) oscillations characteristic of the metallic state persist in 30 nm diameter nanowires. They interpret their results in terms of evanescent surface states dominating the electron structure at small sizes. In other words the surface states increase the carrier density and

the nanowires do not become semiconducting [28]. They further show that the SdH oscillations they find indicate a nearly spherical Fermi surface pocket with a relatively large effective mass. If this is the case, then our even smaller diameter nanorods (~10 nm) should have an even higher density of states and a Fermi surface quite different than that of bulk Bi. If the absorption peaks are due to surface states, then they need not vary as $1/d^2$, and might be quite dependent on the details of the wire orientation and surface structure.

To ascertain that the sharp IR features depicted in Fig. 4.7 are intrinsic to Bi nanorods, we annealed the obtained deposit in air using a tube furnace maintained at 100 °C. A room temperature IR absorption spectrum (see Fig. 4.11) was collected from the annealed sample as a function of the annealing time. As expected, the 1393 cm^{-1} feature begins to lose intensity due to the conversion of the sample to Bi_2O_3 , and this peak completely disappears after an annealing time of 5 hours. This experiment confirmed that the 1393 cm^{-1} peak is due to the Bi nanorods and not Bi_2O_3 .

Figure 4.11: Room temperature IR absorption spectra of Bi nanorods annealed in air for 5 hrs. As annealing time increases, the 1393 cm^{-1} peak intensity decreases.

4.3 UV-Visible Spectroscopy

In UV-visible spectroscopy (UV-vis) light, which can be either visible or ultraviolet, is absorbed by the valence electrons. These electrons are then promoted from their ground states to higher energy states. See Fig. 4.12 for more details. The energies of the electron orbitals involved in the transition have fixed values. This is because there are also vibrational and rotational energy levels available for the material to absorb.

Light absorption occurs over a wide range. In our case, we can detect absorption in the range of 200 – 1200 nm using a Perkin-Elmer Lambda 950 spectrometer. Valence electrons are found in three types of electron orbitals, which are single or (σ bonding orbitals), double or triple (π bonding orbitals), and non-bonding orbitals (lone pair electrons). Sigma (σ) bonding orbitals tend to be lower in energy than π bonding orbitals, which in turn are lower in energy than non-bonding orbitals [62].

Figure 4.12: When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals [62].

One can find the relationship between the energy gap and the wavelength absorbed. We can start with the relationship between the frequency of light absorbed and its energy. This relationship can be seen by the following:

$$E = h \nu \quad (4.5)$$

where E is the energy of the light, h is Planck's constant and ν is the frequency of the light [63]. Looking at Eq. 4.5, one can see that if a high energy jump can result from the absorption of high frequency light. UV-vis absorption spectra are always given using wavelengths of light rather than frequency. The relationship between wavelength and the frequency is given by

$$\lambda = \frac{c}{\nu} \quad (4.6)$$

where λ is the wavelength and c is the speed of light. By looking at the above equation, one can see that the higher the frequency is, the lower the wavelength will be. The most common way to relate the absorption of light to the properties of the material through which the light is traveling is through the Beer-Lambert Law. This relationship is given by

$$A = \log_{10}(I / I_0) = \varepsilon c L \quad (4.7)$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the path length through the sample, ε is the absorption coefficient divide by a constant (2.303) and c the concentration of the absorbing material [63].

To obtain an absorbance spectrum, a sample is placed in the spectrophotometer and ultraviolet or visible light at a certain wavelength, or range of wavelengths, is transmitted through the sample. Most samples are suspensions and are placed in quartz cuvettes. The spectrophotometer measures how much of the light is transmitted by the sample and the fraction of light transmittance (I / I_0), is usually expressed in terms of percent transmittance (%T). From this information, the absorbance of the sample can be determined for a range of wavelengths.

In our UV-visible absorption studies, a UV-visible (model PerkinElmer Lambda 950) spectrometer was used to study the as-prepared Bi nanorods. As a further confirmation for the QCE, we suspended our as-prepared deposit (~3 mg) in ethanol (~10 ml) and measured its UV-visible absorption spectrum. Wang *et al.* [64] recently reported observing a surface plasmon absorption peak at 281 nm (4.4 eV) in 6.5 nm Bi nanoparticles (see Fig 4.13). Figure 4.14 shows the absorption spectrum for the suspended nanorods referenced against blank ethanol solution. The broad peak present at

302 nm (4.1 eV) is due to the surface plasmon absorption. Consistent with the QCE, the surface plasmon peak in the nanorod spectrum is red-shifted relative to the corresponding peak reported for the Bi nanoparticles.

Figure 4.13: UV-visible spectrum of as-prepared Bi nanoparticles with an average diameter of ~ 6.5 nm. A surface plasmon absorption peak is observed at 281 nm [64].

Figure 4.14: UV-visible absorption spectrum shows the as-prepared Bi nanorods suspended in ethanol. An absorption peak is observed at 302 nm or 4.1 eV [59].

CHAPTER 5

SUMMARY

5.1 Conclusions

Highly crystalline bismuth nanorods ~ 10 nm in diameter were prepared using a PLV technique. This method shows clear potential for PLV as a useful technique for obtaining crystalline thermoelectric materials. Theory has shown that the nanorods synthesized in this thesis should exhibit a semiconducting behavior due to their small diameter. Additionally, the small diameters lead to high mobilities and quantum confinement which can provide a higher ZT value, a prerequisite for efficient thermoelectric materials.

Room temperature FTIR spectroscopy is shown to be an excellent tool for characterizing the Bi nanostructures prepared in this study. A blue-shift in the infrared absorption band is observed for the Bi nanorods, and the infrared band is clearly resolved into two main absorption peaks centered around 1393 cm^{-1} and 1460 cm^{-1} . This frequency shift is consistent with a $1/d^2$ behavior as predicted by quantum confinement. Furthermore, the mass of the electron needed for the 1393 cm^{-1} absorption peak can be calculated. We estimate an effective mass component of $0.0433m_o$. To further confirm the QCE in Bi nanorods, a UV-Visible absorption spectrum was measured at room temperature. A broad peak is found at 302 nm (4.1 eV) and is attributed to the surface plasmon absorption which is absent in bulk Bi. Consistent with the QCE, the surface

plasmon peak in the nanorod spectrum is red-shifted relative to the corresponding peak reported for the Bi nanoparticles.

5.2 Future Work

The synthesis process outlined in this thesis is versatile and can be used for synthesizing other thermoelectric (TE) nanostructures such as Bi_2Te_3 , PbTe and $\text{Si}_{1-x}\text{Ge}_x$. BiSb is a new promising TE material and preliminary work to prepare Sb-doped Bi nanorods is in progress. Also, one of our present goals is to prepare Bi nanorods with controlled mean diameter and track its corresponding IR absorption peaks. A low temperature (77 K) FTIR study will be performed using the as-prepared Bi nanorods to see if the peaks in the IR absorption band become narrower and provide further insight to the energy difference of the electronic sub-bands.

REFERENCES

- [1] T. J. Seebeck, *Abh. K. Akad. Wiss. Berlin*, 1823), p. 265.
- [2] J. C. Peltier, *Ann. Chem.* **LVI**, 371 (1834).
- [3] T. M. Tritt, *Recent Trends in Thermoelectronic Materials Research* (Academic Press, New York, 2000), Vol. 69-71.
- [4] A. F. Ioffe, *Semiconductor Thermoelements and thermoelectric Cooling* (Infosearch, London, 1957).
- [5] Y.-M. Lin, X. Sun, and M. S. Dresselhaus, *Phys. Rev. B* **62**, 4610 (2000).
- [6] Y.-M. Lin *et al.*, *Appl. Phys. Lett.* **76**, 3944 (2000).
- [7] N. Mingo, *Appl. Phys. Lett.* **85**, 5986 (2004).
- [8] L. D. Hicks *et al.*, *Phys. Rev. B* **53**, 10493 (1996).
- [9] R. Venkatasubramanian *et al.*, *Nature* **413**, 597 (2001).
- [10] S. Farhangfar, *Phys. Rev. B* **74**, 205318 (2006).
- [11] S. B. Cronin *et al.*, in *21st International Conference on Thermoelectrics* (2002), p. 243.
- [12] R. T. Isaacson, and G. A. Williams, *Phys. Rev.* **185**, 682 (1969).
- [13] G. Dresselhaus *et al.*, in *International Conference on Thermoelectrics* (IEEE, Piscataway, NJ, Nagoya, Japan, 1998), p. 43.
- [14] M. R. Black *et al.*, *Phys. Rev. B* **65**, 195417 (2002).
- [15] T. M. Tritt, and M. A. Subramanian, *MRS Bulletin* **31** (2006).
- [16] H. J. Goldmid, *Thermoelectric Refrigeration* (Plenum, New York, 1964).
- [17] L. D. Hicks, and M. S. Dresselhaus, *Phys. Rev. B* **47**, 16631 (1993).
- [18] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor and Francis, London, 1972).

- [19] R. Eisberg, and R. Resnick, *Quantum Physics* (John Wiley & Sons, Inc., 1985), p. 384.
- [20] T. W. Cornelius *et al.*, Appl. Phys. Lett. **88**, 103114 (2006).
- [21] X. Sun, Z. Zhang, and M. S. Dresselhaus, Appl. Phys. Lett. **74**, 4005 (1999).
- [22] C. A. Hoffman, J. R. Meyer, and F. J. Baroli, Phys. Rev. B **48**, 11431 (1993).
- [23] M. R. Black *et al.*, Phys. Rev. B **68**, 235417 (2003).
- [24] M. S. Dresselhaus *et al.*, Mat. Science and Eng. C **23**, 129 (2003).
- [25] D. M. Rowe, *Thermoelectrics Handbook: Macro to Nano* (Taylor and Francis, New York, 2006).
- [26] J. Heremans *et al.*, Phys. Rev. B **61**, 2921 (2000).
- [27] W. M. Wang *et al.*, Appl. Phys. Lett. **88**, 143106 (2006).
- [28] T. E. Huber *et al.*, Appl. Phys. Lett. **84**, 1326 (2004).
- [29] T. W. Cornelius *et al.*, Nanotechnology **16**, S246 (2005).
- [30] J. P. Heremans *et al.*, Phys. Rev. Lett. **88**, 216801 (2002).
- [31] Z. Hu, G. Oskam, and P. C. Searson, J. Colloid and Inter. Science **263**, 454 (2003).
- [32] L. E. Brus, J. Phys. Chem. **90**, 2555 (1986).
- [33] K. McGuire, in *Physics and Astronomy* (Ph.D. Thesis, Clemson University, Clemson, SC, 2003).
- [34] L. I. Berger, *Semiconductor Materials*, CRC, Boca Raton, FL, 1997).
- [35] M. S. Gudiksen, J. Wang, and C. M. Lieber, J. Phys. Chem. B **106**, 4036 (2002).
- [36] G. B. Arfken, and H. J. Weber, *Mathematical Methods for Physicists* (Academic Press, San Diego, 1995).
- [37] A. M. Morales, and C. M. Lieber, Science **279**, 208 (1998).
- [38] Y. Wu, and P. Yang, Chem. Mater. **12**, 605 (2000).

- [39] Q. Wei, and C. M. Lieber, *Mat. Res. Soc. Symp. Proc.* **581**, 219 (2000).
- [40] K.-K. Lew *et al.*, *Adv. Mater.* **15**, 2073 (2003).
- [41] C. R. Martin, *Science* **266**, 1961 (1994).
- [42] B. Zhang, J. He, and T. M. Tritt, *Appl. Phys. Lett.* **88**, 043119 (2006).
- [43] L. Shi, C. Yu, and J. Zhou, *J. Phys. Chem. B* **109**, 22102 (2005).
- [44] D. Wang, and H. Dai, *Angew. Chem. Int. Ed.* **41**, 4783 (2002).
- [45] *The Chemistry of Nanomaterials* (WILEY-VCH Verlag GmbH & Co., KagA, Weiheim, 2004), Vol. 1.
- [46] T. J. Groshens, R. W. Gedridge, and C. Lowe-Ma, *Chem. Mater.* **6**, 727 (1994).
- [47] J. J. Ritter, *Inorg. Chem.* **33**, 6419 (1994).
- [48] Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).
- [49] J. Reppert *et al.*, *Chem. Phys. Lett.* **442**, 334 (2007).
- [50] C. N. R. Rao *et al.*, *Chem. Phys. Chem.* **2**, 78 (2001).
- [51] R. S. Wagner, and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).
- [52] M. S. Gudiksen, and C. M. Lieber, *J. Am. Chem. Soc.* **122**, 8801 (2000).
- [53] X. Duan, and C. M. Lieber, *Adv. Mater.* **12**, 298 (2000).
- [54] X. Duan, and C. M. Lieber, *Adv. Mater.* **12**, 298 (2000).
- [55] P. Y. Chevalier, *Thermochinica Acta* **136**, 15 (1988).
- [56] N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Intro. to Infrared and Raman Spectroscopy* (Academic Press, New Youk, 1964).
- [57] P. R. Griffiths, and J. A. d. Haseth, *Fourier Transfrom Infrared Spectroscopy* (John Wiley & Sons, 1986), Vol. 83.
- [58] B. C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy* (CRC press, Boca Raton, 1996).

- [59] J. Reppert *et al.*, Chem. Phys. Lett. (submitted).
- [60] J. Heremans, and O. P. Hansen, J. Phys. C **12**, 3483 (1979).
- [61] W. Wang *et al.*, Adv. Mater. **17**, 2110 (2005).
- [62] C. B. Faust, *Modern Chemical Techniques* (RCS, 1992).
- [63] K. Hirayama, *Handbook of UV & Visible Absorption Spectra of Organic Compounds* (Plenum Press., 1967).
- [64] Y. M. Wang, B. Y. Hong, and K. S. Kim, J. Phys. Chem. B **109**, 7067 (2005).