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Experimental and Theoretical Investigation of Thermal and Thermoelectric Transport in Nanostructures

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Experimental and Theoretical Investigation of Thermal and Thermoelectric Transport in Nanostructures

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Dedication

To my parents, Bob and Ann, my darling daughter, Emma, and to my loving wife Mary, without whom this would not have been possible.
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Experimental and Theoretical Investigation of Thermal and Thermoelectric Transport in Nanostructures

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This work presents the development and application of analytical, numerical, and experimental methods for the study of thermal and electrical transport in nanoscale systems, with special emphasis on those materials and phenomena which can be important in thermoelectric and semiconductor device applications. Analytical solutions to the Boltzmann transport equation (BTE) using the relaxation time approximation (RTA) are presented and used to study the thermal and electrical transport properties of indium antimonide (InSb), indium arsenide (InAs), bismuth telluride (Bi$_2$Te$_3$), and chromium disilicide (CrSi$_2$) nanowires. Experimental results for the thermal conductivity of single layer graphene supported by SiO$_2$ were analyzed using an RTA-based model and compared to a full quantum mechanical numerical BTE solution which does not rely on the RTA. The ability of these models to explain the measurement results as well as differences between the two approaches are discussed. Alternatively, numerical solutions...
to the BTE may be obtained statistically through Monte Carlo simulation for complex geometries which may prove intractable for analytical methods. Following this approach, phonon transport in silicon (Si) sawtooth nanowires was studied, revealing that thermal conductivity suppression below the diffuse surface limit is possible.

The experimental investigation of energy transport in nanostructures typically involved the use of microfabricated devices or non-contact optical methods. In this work, two such approaches were analyzed to ascertain their thermal behavior and overall accuracy as well as areas for possible improvement. A Raman spectroscopy-based measurement design for investigating the thermal properties of suspended and supported graphene was examined analytically. The resulting analysis provided a means of determining from measurement results the thermal interface conductance, thermal contact resistance, and thermal conductivity of the suspended and supported graphene regions. Previously, microfabricated devices of several different designs have been used to experimentally measure the thermal transport characteristics of nanostructures such as carbon nanotubes, nanowires, and thin films. To ascertain the accuracy and limitations of various microdevice designs and their associated conduction analyses, finite element models were constructed using ANSYS and measurements of samples of known thermal conductance were simulated. It was found that designs with the sample suspended were generally more accurate than those for which the sample is supported on a bridge whose conductance is measured separately. The effects of radiation loss to the environment of certain device designs were also studied, demonstrating the need for radiation shielding to be at temperatures close to that of the device substrate in order to accurately calibrate the resistance thermometers.
Using a suspended microdevice like those analyzed using finite element analysis, the thermal conductivities of individual bismuth (Bi) nanowires were measured. The results were correlated with the crystal structure and growth direction obtained by transmission electron microscopy on the same nanowires. Compared to bulk Bi in the same crystal direction, the thermal conductivity of a single-crystal Bi nanowire of 232 nm diameter was found to be 3 - 6 times smaller than bulk between 100 K and 300 K. For polycrystalline Bi nanowires of 74 nm to 255 nm diameter the thermal conductivity was reduced by a factor of 18 - 78 over the same temperature range. Comparable thermal conductivity values were measured for polycrystalline nanowires of varying diameters, suggesting a grain boundary scattering mean free path for all heat carriers in the range of 15 - 40 nm which is smaller than the nanowire diameters. An RTA-based transport model for both charge carriers and phonons was developed which explains the thermal conductivity suppression in the single-crystal nanowire by considering diffuse phonon-surface scattering, partially diffuse surface scattering of electrons and holes, and scattering of phonons and charge carriers by ionized impurities such as oxygen and carbon of a concentration on the order of $10^{19}$ cm$^{-3}$.

Using a similar experimental setup, the thermoelectric properties (Seebeck coefficient, electrical conductivity, and thermal conductivity) of higher manganese silicide (HMS) nanostructures were investigated. Bulk HMS is a passable high temperature thermoelectric material which possesses a complex crystal structure that could lead to very interesting and useful nanoscale transport properties. The thermal conductivities of HMS nanowires and nanoribbons were found to be reduced by 50 – 60 % compared to bulk values in the same crystal direction for both nanoribbons and
nanowires. The measured Seebeck coefficient data was comparable or below that of bulk, suggesting unintentional doping of the samples either during growth or sample preparation. Difficulty in determining the amorphous oxide layer thickness for nanoribbons samples necessitated using the total, oxide-included cross section in the thermal and electrical conductivity calculation. This in turn led to the determined electrical conductivity values representing the lower bound on the actual electrical conductivity of the HMS core. From this approach, the measured electrical conductivity values were comparable or slightly below the lower end of bulk electrical conductivity values. This oxide thickness issue affects the determination of the HMS nanostructure thermoelectric figure of merit $ZT$ as well, though the lower bound values obtained here were found to still be comparable to or slightly smaller than the expected bulk values in the same crystal direction. Analytical modeling also indicates higher doping than in bulk. Overall, HMS nanostructures appear to have the potential to demonstrate measurable size-induced $ZT$ enhancement, especially if optimal doping and control over the crystallographic growth direction can be achieved. However, experimental methods to achieve reliable electrical contact to quality four-probe samples needs to be improved in order to fully investigate the thermoelectric potential of HMS nanostructures.
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Chapter 1: Introduction

The need to study thermal transport at the micro- and nanoscale first became apparent with the progressive miniaturization of integrated circuits (ICs) as a means of increasing computing power and minimizing per unit cost. Figure 1.1 shows the continued reduction of the minimum IC feature size over the past twenty-five years (ICKnowledge 2008), with sub-100 nm devices appearing commercially in 2002-2003 and sub-45 nm technology currently in development (ITRS 2010).

Figure 1.1: Decreasing minimum feature size and increasing transistor density of Intel microprocessor technology over time. Original data from ICKnowledge (ICKnowledge 2008).
The decrease in feature size and associated increase in transistor density has led to new challenges in electronics thermal management. As the size of transistors, thin film layers, and interconnects decreases, their electrical conductivity (Fishman and Calecki 1989; Liu, Zhao et al. 2001; Barnat, Nagakura et al. 2002; Graham, Alers et al. 2010) and thermal conductivity (Ju and Goodson 1999; Ju, Kurabayashi et al. 1999; Yang, Liu et al. 2004) decrease as well, leading to greater power dissipation and a reduced ability to conduct heat away from the device. Combined with a rising number of layers and interfaces as well as increasing transistor density, the result is higher heat densities and increased operating temperatures which can lead to performance-compromising effects such as current leakage, shortened device lifetime, and inefficient power management (Schelling, Shi et al. 2005; Lin and Banerjee 2008).

To complicate matters, the localized nature of IC architectures often makes the heat being generated non-uniform in nature, forming specific regions of high temperature know as “hot spots” which ultimately determine the required amount of cooling rather than the average die temperature (Mahajan, Chiu et al. 2006; Lin and Banerjee 2008). Thus, in order for the full technological and economic benefits of decreasing feature size to be realized, a thorough understanding of thermal transport and management at the nanoscale must also be developed. This includes the study of nanoscale thermal contact resistance (Shi and Majumdar 2002; Yovanovich 2005; Hu, Keblinski et al. 2008), geometric effects in nanoscale thermal constrictions (Bahadur, Xu et al. 2005; Prasher 2005; Saha and Shi 2007; Zhang, Mingo et al. 2007), and thermal transport through potential next generation computing elements such as nanowires (Li, Wu et al. 2003; Zhou, Szczech et al. 2007; Zhou, Moore et al. 2010), nanotubes (Kim, Shi et al. 2001;
Shi, Li et al. 2003; Yu, Shi et al. 2005; Pettes and Shi 2009), and graphene (Balandin, Ghosh et al. 2008; Cai, Moore et al. 2010; Seol, Jo et al. 2010).

The drive for research into nanoscale heat transfer has also been brought about by interest in nanostructured materials for thermoelectric energy conversion. Thermoelectric materials are used to accomplish one of two energy conversion functions: 1) power generation using a temperature gradient, or 2) solid-state refrigeration via an applied electric field. In either application, one may express the efficiency of the energy conversion in terms of the transport coefficients for the constituent thermoelectric materials. The figure of merit $ZT$ for a thermoelectric material is given by

\[ ZT = \frac{S^2 \sigma}{\kappa} T \]  

(1.1)

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the total thermal conductivity, and $T$ is the absolute temperature (Rowe 1994). The total thermal conductivity $\kappa$ consists of contributions from phonons ($\kappa_{ph}$), electrons ($\kappa_e$), holes ($\kappa_h$), and bipolar diffusion ($\kappa_{eh}$) such that $\kappa = \kappa_{ph} + \kappa_e + \kappa_h + \kappa_{eh}$. Increasing the $ZT$ of bulk materials is often challenging due to the interconnecting relationships between $S$, $\sigma$, and the electronic contributions to $\kappa$ (Majumdar 2004; Li, Huxtable et al. 2005; Tritt and Subramanian 2006). For a thermoelectric cooler to have efficiencies competitive with conventional compressor-based refrigeration units, it must have $ZT$ of 3 or greater (Li, Huxtable et al. 2005). Most bulk thermoelectric materials in use today have a peak $ZT$ comparable to or less than unity and operate in a specific temperature range (Tritt and Subramanian 2006). For applications in the near-ambient temperature range ($200 \text{ K} < T$
< 500 K), bismuth telluride (Bi₂Te₃) and its alloys with antimony are the most commonly used materials with a typical ZT value of around 0.9-1.0 near 300 K (Rowe 1994). Other common materials are metal oxides and silicides as well as certain semiconductor alloys such as silicon germanium (Si₁₋ₓGeₓ) (Tritt and Subramanian 2006).

Beginning in the mid 1990s and early 2000s, theoretical analysis of size effects on the thermal and electrical properties of materials began predicting an enhancement in ZT for one-dimensional (1D) and two-dimensional (2D) nanostructures such as nanowires and thin film superlattices, especially those comprised of bismuth-based materials (Hicks and Dresselhaus 1993; Hicks and Dresselhaus 1993; Hicks, Harman et al. 1993; Lin, Sun et al. 2000; Rabin, Lin et al. 2001) and III-V (Koga, Sun et al. 1998; Mingo 2004; Mingo 2006). This predicted enhancement originates from three potential sources: 1) for characteristic lengths comparable to the energy carrier mean free path, the increased importance of carrier-boundary/interface scattering suppresses the thermal conductivity, 2) for sufficiently small structures comparable to the charge carrier’s wavelength, quantum confinement effects change the nature of the charge carrier density of states, thereby leading to possible enhancement of the power factor (S²σ), and 3) for characteristic lengths comparable to the dominant phonon wavelength, the allowable phonon wavevectors change, thereby altering the dispersion relationship between phonon wavelength and wavevector in the nanostructure. This last size effect can alter the phonon group velocity, density of states, and mean free path due to phonon-phonon scattering, further reducing the lattice component κₚₚ of the thermal conductivity.

As the above discussion illustrates, the term “size effects” encompasses many different phenomena in small scale physics. The nature and relative impact of size
effects on energy transport varies depending on the material system, characteristic
dimensions involved, important length scales, and the dominant carrier type present.
Classical size effects include those for which the energy carrier (either phonons or charge
carriers) and their behavior can still be described as particle-like. This corresponds to the
first effect discussed above with regards to thermoelectric nanostructures. The most
common example is when the bulk carrier mean free path is comparable to or larger than
the characteristic dimension of the nanostructure such that increased carrier-boundary
scattering occurs. Thus, the relative impact of carrier-boundary scattering on the overall
transport characteristics of the nanostructure depends on the mean free path of a given
energy carrier and its relative contribution to the overall transport.

Quantum size effects include those for which the wave-like nature of an energy
carrier is affected by size-induced confinement. These correspond to the second and third
size effects discussed above for thermoelectric nanostructures. For both charge carriers
and phonons, the onset of quantum confinement occurs when the characteristic dimension
of the nanostructure is comparable to the carrier’s wavelength rather than its mean free
path. The confinement changes the wave nature of the carrier, altering its density of
states, available energy levels, and other properties according to the specific material
system and the degree of confinement. Like the carrier mean free path, the important
carrier wavelengths vary between material systems and can be a function of both
temperature and Fermi level, making the choice of material system with which to study
quantum size effects very important.

The realization of $ZT$ enhancement by quantum size effects is challenging
experimentally as well as restricted to specific material systems under specific conditions
such as small carrier effective mass, low temperatures, and/or exceedingly small dimensions of a few nanometers. Within the operating temperature range of most potential thermoelectric devices, the energy carrier mean free paths are typically much longer (tens or hundreds of nanometers) than the carrier wavelength (a few nanometers or less). Due to these factors, the experimental observation of quantum confinement-induced $ZT$ enhancement has remained elusive for researchers. Though not size-induced, a distorted density of states approach similar to that desired from quantum confinement was achieved in thallium (Tl)-doped bulk lead telluride (PbTe), increasing the $ZT$ to above 1.6 at 773 K (Heremans, Jovovic et al. 2008).

Instead, the approach of many researchers has been to attempt to reduce the phonon thermal conductivity $\kappa_{ph}$ via phonon-boundary or phonon-interface scattering. The requirement of a large $S$ for high $ZT$ means that most thermoelectric materials are doped semiconductors and thus possess a large or even dominant $\kappa_{ph}$ contribution to the total thermal conductivity $\kappa$. Thus, a significant reduction in $\kappa_{ph}$ while minimizing any negative impact on the power factor $S^2\sigma$ would increase $ZT$ above the bulk value.

This approach has been taken in thin film superlattices (Lee, Cahill et al. 1997; Venkatasubramanian, Siivola et al. 2001; Beyer, Nurnus et al. 2002; Yang, Liu et al. 2002), nanoparticle-embedded composites (Kim, Singer et al. 2006; Kim, Zide et al. 2006; Yang, Hng et al. 2009), nanowires (Zhou, Jin et al. 2005; Zhou, Szczech et al. 2007; Boukai, Bunimovich et al. 2008; Hochbaum, Chen et al. 2008; Mavrokefalos, Moore et al. 2009; Zhou, Moore et al. 2010), and nanostructured bulk materials (Joshi, Lee et al. 2008; Ma, Hao et al. 2008; Poudel, Hao et al. 2008). While all of these
approaches have demonstrated low or suppressed $\kappa$, in many studies the power factor is also reduced due to strong boundary scattering of charge carriers or unintentional doping during synthesis, thus preventing or limiting $ZT$ enhancement (Beyer, Nurnus et al. 2002; Seol, Moore et al. 2007; Mavrokefalos, Moore et al. 2009; Zhou, Moore et al. 2010). The addition of semimetallic ErAs nanoparticles to In$_{0.53}$Ga$_{0.47}$As was found to both reduce the thermal conductivity by a factor of two and increase the $ZT$ by a factor of two, with the nanoparticles acting as dopants as well as phonon scattering centers (Kim, Zide et al. 2006). In another approach to achieving high $ZT$ via classical size effects, bulk materials such as bismuth-antimony-tellurium alloys (BiSbTe) (Ma, Hao et al. 2008; Poudel, Hao et al. 2008), silicon (Si) (Bux, Blair et al. 2009), or SiGe (Joshi, Lee et al. 2008) are ball-milled into nanoparticles and hot pressed at a given temperature, pressure, and composition. The nanoparticles fuse together but retain their boundaries, forming a bulk-sized sample with a nanograined structure (Minnich, Dresselhaus et al. 2009). The grain boundaries act to scatter phonons as they travel through the material, thereby reducing $\kappa_{ph}$. In terms of electrical transport, because the material is the same on either side of the grain boundary there is no bandgap offset and the scattering of charge carriers by the grain boundaries is less severe than in superlattices of alternating materials or from nanowire boundaries (Minnich, Dresselhaus et al. 2009). The end result is a nanograin bulk material with enhanced $ZT$ compared to single crystal samples, achieving peak $ZT$ values of 1.4 at 373 K for BiSbTe (Poudel, Hao et al. 2008), 0.69 at 1100 K for Si (Bux, Blair et al. 2009), and 1.0 at 1073 K for SiGe (Joshi, Lee et al. 2008). However, thermoelectric materials are expected to perform at elevated temperatures for extended
periods of time, which in the case of nanograined thermoelectrics would lead to progressive grain growth and decreased performance (Minnich, Dresselhaus et al. 2009).

The areas of electronics cooling and thermoelectric refrigeration are connected by more than just the study of nanoscale thermal transport. The solid state refrigeration capabilities offered by thermoelectrics are attractive for cooling local hot spots of semiconductor devices especially in terms of reliability (Mahajan, Chiu et al. 2006). However, the low efficiency and inherently thick nature of current commercial thermoelectric coolers makes most thermoelectric modules incompatible with IC packaging designs (Mahajan, Chiu et al. 2006; Chowdhury, Prasher et al. 2009). The use of thin films, nanowires, or nanotubes could potentially be used as active elements in a thinner, more efficient thermoelectric module for site-specific cooling of hot spots in microprocessor or other electronic and optoelectronic devices (Chowdhury, Prasher et al. 2009). The use of a thin film superlattice-based thermoelectric module to perform on-chip cooling has already been demonstrated in prototype form, achieving local cooling of 15°C (Chowdhury, Prasher et al. 2009). Using nanomaterials with higher $ZT$ would allow for even greater cooling capabilities with multiple thermoelectric coolers being available for use at various locations as thermal demand changes.

It is the purpose of this work to investigate size effects on charge carriers and phonons involved in thermal and thermoelectric transport at the nanoscale, with special emphasis on those materials and phenomena which might be important in thermoelectric and semiconductor device applications. The major components of this work are i) the development and implementation of analytical and numerical methods for analyzing nanoscale energy transport from experimental data, ii) analytical and numerical
evaluation of experimental methods for the measurement of the transport properties of nanostructures, and iii) the measurement and analysis of thermal and thermoelectric transport in Bi and higher manganese silicide (HMS) nanostructures. The specific organization of the dissertation is as follows:

In Chapter 2, analytical and numerical methods are employed in the analysis and simulation of nanoscale energy transport. The Boltzmann transport equation (BTE) is discussed, as well as analytical means for obtaining the thermoelectric transport coefficients $S$, $\sigma$, and $\kappa$ using the BTE with the relaxation time approximation (RTA). These expressions are used to analyze the measured thermal and electrical transport properties of indium antimonide (InSb), indium arsenide (InAs), bismuth telluride ($\text{Bi}_2\text{Te}_3$), and chromium disilicide ($\text{CrSi}_2$) nanowires, providing insight into the nanowires’ mobilities and doping levels that would be difficult or impossible to obtain otherwise. An RTA-based analytical BTE model is also used to examine phonon transport in single-layer graphene supported on silicon dioxide ($\text{SiO}_2$). The results for the thermal conductivity of supported graphene from a non-RTA numerical solution of the BTE are compared to those obtained using the RTA-based analytical model and differences are discussed. Statistical solution of the BTE via Monte Carlo simulation was used to study phonon transport in Si sawtooth nanowires.

Chapter 3 evaluates several measurement methods used for studying energy transport in nanostructures. An analytical evaluation of a Raman spectroscopy-based optical measurement approach for determining the thermal properties of suspended and supported graphene is presented. In addition, finite element models of several suspended
microdevices are presented and their respective thermal characteristics discussed in relation to their respective conduction analyses.

Chapter 4 details the measurement and analysis of thermal transport in individual Bi nanowires. Thermal transport in bulk Bi is reviewed and the potential impact of size effects on both charge carriers and phonons is discussed. Synthesis by vapor deposition of Bi into the nanopores of anodic alumina templates is described. Measurements performed using a microfabricated device within a vacuum-pumped cryostat are detailed and the results presented. A multi-carrier analytical model based on the methods developed in Chapter 2 is offered as a means of interpreting the measurement results.

In Chapter 5, aspects of the HMS crystal structure are discussed in term of their impact on the thermoelectric potential of HMS nanostructures. The thermoelectric properties of HMS nanostructures are evaluated using both suspended and substrate-based microdevices. The measurement results are correlated with transmission electron microscopy (TEM) analysis in terms of growth direction and the specific HMS phase. Comparisons to transport in bulk HMS are made, with special emphasis on the potential of HMS nanostructures to achieve high ZT.

The major findings of this work are summarized in Chapter 6.
Chapter 2: Analytical and Numerical Modeling of Nanoscale Energy Transport

Though still challenging, measurements of nanowires, nanotubes, and thin film transport properties have become familiar within academic literature. These include the thermoelectric transport coefficients $S$, $\sigma$, and $\kappa$, of which $\sigma$ is the most commonly seen and $\kappa$ regarded as the most difficult to measure. Beyond direct measurement of the transport coefficients, further information regarding doping level, carrier mobility, dominant scattering mechanism, sample quality, etc. is crucial to fully understanding the measured properties and guiding development towards improved performance. These insights are sometimes difficult or impossible to obtain experimentally for nanostructures. For example, Hall measurements which can provide information on carrier concentration and mobility are unattainable on nanowires and nanotubes due to their 1D geometry conflicting with the necessary measurement configuration. Though nanowire mobility may be measured using the experimentally complex Shubnikov-de Hass (SdH) method (Heremans, Thrush et al. 2002), this approach is limited to nondegenerate nanowires only. As will be shown, in many cases thermoelectric nanowires are degenerately doped, rendering the SdH method not applicable. Alternatively, nanowire mobility may be deduced from field effect measurements, but the presence of a gate and dielectric conflict with thermal conductivity experimental
configurations. In addition mobility determination from field effect measurements do not work for highly doped nanowires and suffer from uncertainty in the gate capacitance.

In some cases, however, analytical modeling can be used to shed light on the important carrier dynamics and provide information not explicitly shown in the measurement data alone. In this chapter, analytical and numerical methods of simulating nanoscale energy transport are developed to obtain important information related to carrier behavior. Analytical methods are employed to analyze measured nanostructure transport property data, while numerical simulations are used to further understanding of thermal transport in geometrically complex nanostructures.

The appropriate means by which energy transport at small scales is modeled depends greatly on the particular system under study. First and foremost, one must decide whether the energy carriers should be modeled as waves with phase and interference effects considered or as particles. One means of determining the importance of wave effects is based on a comparison of the carrier’s relevant wavelengths (de Broglie wavelength for electrons, dominant thermal wavelength for phonons) and the characteristic dimensions of the system. The choice is not always clear as the demarcation between transport regimes is not abrupt (Chen, Borca-Tasciuc et al. 2004). In general, wave effects can be safely neglected if the characteristic length is larger than the carrier’s relevant wavelengths. A similar length scale comparison should be made between the phase coherence length of the carrier and the characteristic length. With this comparison in mind, the occurrence of phase-destroying scattering processes should be considered. Phase-destroying processes render wave effects unobservable, in which case such effects can be safely disregarded. Diffuse scattering from a rough surface or
inelastic scattering processes such electron-phonon or phonon-phonon interactions are considered phase destroying (Chen, Borca-Tasciuc et al. 2004). These are quite prevalent in thermoelectric nanowires or semiconductor nanostructures with etched boundaries. Due to the dimensions of the nanostructures under investigation (tens of nanometers or more), the relevant carrier wavelengths, and the significant presence of phase-destroying processes, phonons and charge carriers are modeled as particles in this work using equations derived from the BTE. Specific justifications for this choice are made in more detail throughout the following chapter.

**The Boltzmann Transport Equation**

A brief review of the BTE and RTA is given here in order to facilitate full discussion of the limitations of RTA-based models later in this work. Full details can be found in many solid state physics texts (Ziman 1962; Ashcroft and Mermin 1976; Chen 2005). Consider a dilute system of particles where the probability of finding a particle at location \( \vec{r} \) with wavevector \( \vec{k} \) at time \( t \) is given by the distribution function \( f(\vec{r}, \vec{k}, t) \). If the system is at equilibrium with no applied force fields or temperature gradients, then \( f(\vec{r}, \vec{k}, t) \) becomes the equilibrium distribution function \( f_0(\vec{r}, \vec{k}, t) \). Electrons follow Fermi-Dirac statistics for which \( f_0(\vec{r}, \vec{k}, t) \) is given by the Fermi-Dirac distribution

\[
f_0(\vec{r}, \vec{k}, t) = \frac{1}{e^{(E-E_F)/k_B T} + 1}
\]  

(2.1)

while for holes the equilibrium distribution is
\begin{equation}
    f_0(\vec{r}, \vec{k}, t) = 1 - \frac{1}{e^{(E-E_F)/k_BT} + 1}
\end{equation}

where \( E \) is energy, \( E_F \) is the Fermi level, and \( k_B \) is the Boltzmann constant (Ashcroft and Mermin 1976). In the equilibrium case, \( f_0(\vec{r}, \vec{k}, t) \) for electrons or holes depends only on energy with the relationship between \( E \) and \( \vec{k} \) given by the band structure of the material.

Phonons follow Bose-Einstein statistics for which \( f_0(\vec{r}, \vec{k}, t) \) is given by the Bose-Einstein distribution

\begin{equation}
    f_0(\vec{r}, \vec{k}, t) = \frac{1}{e^{\hbar \omega/k_BT} - 1}
\end{equation}

where \( \hbar \) is the reduced Planck constant and \( \omega \) is the phonon frequency (Chen 2005). In the equilibrium case, \( f_0(\vec{r}, \vec{k}, t) \) for phonons depends only on frequency with the relationship between \( \omega \) and \( \vec{k} \) given by the phonon dispersion relation. While the equilibrium distributions are usually written as \( f_0(E) \) for charge carriers and \( f_0(\omega) \) for phonons with temperature dependence inherently understood for both, to maintain generality the respective equilibrium distributions will remain written simply as \( f_0(\vec{r}, \vec{k}, t) \) for now.

The BTE is essentially a conservation equation for a dilute system of particles, stating that at steady state there is no net change in the distribution function \( f(\vec{r}, \vec{k}, t) \) due to diffusion through the region of space \( \vec{r} \), interactions with a force field, or scattering processes (Ziman 1962). In equation form
\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} + \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ diffusion}} + \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ forces}} + \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ scattering}} = 0. \quad (2.4)
\]

The diffusion term is usually rewritten as
\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ diffusion}} = -\vec{v}(\vec{k}) \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial \vec{r}} \quad (2.5)
\]

and the force field term rewritten as
\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ forces}} = -\frac{\partial \vec{k}}{\partial t} \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \quad (2.6)
\]

which, following substitution into Equation 2.4, gives the well-known form of the BTE (Chen 2005)
\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} + \frac{\partial \vec{v}(\vec{k})}{\partial \vec{r}} \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial \vec{k}} = \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t \text{ scattering}}. \quad (2.7)
\]

The first term on the left of Equation 2.7 gives the explicit time dependence of the distribution function. The entire left hand side of Equation 2.7 is known as the drift term and the right hand side known as the scattering or collision term. The scattering term is not a true derivative, but serves only to represent the net rate of particles transitioning into the given state via scattering processes (Chen 2005).

There are limits to the validity of the BTE. Due to assumptions inherent in the derivation of the BTE from the Liouville equation, the BTE is appropriate only for dilute systems in which the inter-particle interactions are weak except for those represented in the scattering term (Chen 2005). Such systems include electron or phonon gases, both of which are of interest in this work. In addition, while the BTE can be used for particles
with wave characteristics (frequency, dispersion, etc.) such as phonons, it does not explicitly include wave effects such as interference or tunneling (Chen 2005). This limits the BTE to the description of particle transport and is thus subject to situations where such a treatment is appropriate as discussed at the beginning of this chapter.

Knowledge of the distribution function \( f(\vec{r}, \vec{k}, t) \) allows for calculation of various transport coefficients including \( S, \sigma, \) and \( \kappa \) as will be presented shortly. First, however, Equation 2.7 must be solved for \( f(\vec{r}, \vec{k}, t) \). The handling of the scattering term on the right hand side is critical. One approach is to use the perturbation treatment from quantum mechanics along with Fermi’s golden rule to determine the scattering probability between two states (Ziman 1962; Chen, Borca-Tasciuc et al. 2004; Chen 2005). The scattering integral is then written in terms of the distribution function and the scattering probability, making Equation 2.7 into an integral-differential equation which is quite difficult to solve (Ziman 1962; Chen, Borca-Tasciuc et al. 2004; Chen 2005). More commonly, assumptions and approximations are used which make solution of the BTE more tractable. First, the deviation of the distribution \( f(\vec{r}, \vec{k}, t) \) from the equilibrium distribution \( f_0(\vec{r}, \vec{k}, t) \) is assumed to be small, allowing for the linearization

\[
f(\vec{r}, \vec{k}, t) = f_0(\vec{r}, \vec{k}, t) + f_1(\vec{r}, \vec{k}, t)
\]  

(2.8)

where \( f_1(\vec{r}, \vec{k}, t) \) is the perturbation away from equilibrium (Ziman 1962; Ashcroft and Mermin 1976). Since using this assumption in the BTE leads to linear transport coefficients as are almost always observed in experiment, this approximation is generally viewed as valid (Ziman 1962). Second, it is assumed that scattering processes return the
perturbed system back to the equilibrium distribution exponentially with a relaxation time \( \tau \) such that the scattering term in Equation 2.7 may be written as (Ashcroft and Mermin 1976)

\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} \bigg|_{\text{scattering}} = -\frac{f(\vec{r}, \vec{k}, t) - f_0(\vec{r}, \vec{k}, t)}{\tau} = -\frac{f_1(\vec{r}, \vec{k}, t)}{\tau}.
\]  

Equation 2.9 is the relaxation time approximation (RTA) and is extensively used in the modeling of material transport properties. In reality, \( \tau \) is a function and not a constant but has been written as simply a symbol to preserve generality between both charge carriers and phonons. Additionally, in a strict sense the RTA is only valid for elastic scattering processes such as from impurities or smooth boundaries and not for inelastic processes such as phonon-phonon or electron-phonon scattering (Chen 2005). Regardless, solutions to the BTE utilizing the RTA are widely used even in situations with inelastic scattering and usually achieve acceptable end results (Chen 2005).

Rewriting the BTE with the RTA included gives

\[
\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} + \vec{v}(\vec{k}) \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial \vec{k}} = -\frac{f(\vec{r}, \vec{k}, t) - f_0(\vec{r}, \vec{k}, t)}{\tau}.
\]  

Using the approximation in Equation 2.8 throughout, the equation becomes

\[
\frac{\partial f_1(\vec{r}, \vec{k}, t)}{\partial t} + \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial t} + \vec{v}(\vec{k}) \frac{\partial f_1(\vec{r}, \vec{k}, t)}{\partial \vec{r}} + \vec{v}(\vec{k}) \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f_1(\vec{r}, \vec{k}, t)}{\partial \vec{k}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{k}}...
\]  

\[
= -\frac{f_1(\vec{r}, \vec{k}, t)}{\tau}.
\]  

Three assumptions are used to frame Eq 2.11 in a form from which the transport coefficients may be found (Chen 2005). First, it is assumed that the transient terms are
negligible which removes the first two terms of Equation 2.11. Since thermoelectric transport is only of practical interest in the steady state, this is acceptable. Next, it is assumed that \( f_1(\vec{r}, \vec{k}, t) \ll f_0(\vec{r}, \vec{k}, t) \). This assumption is actually the same as that made in the use of Equation 2.8 that the perturbation from equilibrium was small. Finally, the assumption is made that the gradient in the perturbed term \( f_1(\vec{r}, \vec{k}, t) \) is much smaller than the gradient of the equilibrium distribution \( f_0(\vec{r}, \vec{k}, t) \). This follows a similar argument as the preceding assumption and removes the derivatives involving \( f_1(\vec{r}, \vec{k}, t) \). Using these assumptions and solving for the perturbed distribution gives

\[
f_1(\vec{r}, \vec{k}, t) = -\tau \left( \vec{v}(\vec{k}) \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \right). \tag{2.12}
\]

Since we are interested in the distribution function \( f(\vec{r}, \vec{k}, t) \), Equation 2.12 is used with Equation 2.8 to give the final result (Chen 2005)

\[
f(\vec{r}, \vec{k}, t) = f_0(\vec{r}, \vec{k}, t) - \tau \left( \vec{v}(\vec{k}) \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f_0(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \right). \tag{2.13}
\]

It is this linearized form of the BTE that will be used in the following sections to analyze thermoelectric transport in nanowires and thermal transport in supported graphene.

**ELECTRICAL TRANSPORT MODELING USING THE BTE**

Using the expression in Equation 2.13, relations for the thermoelectric transport coefficients may be obtained by considering the net flux of energy carriers under an electrical potential gradient, a temperature gradient, or both. The purpose of this section is to briefly illustrate how this is done for the electrical terms (\( S \) and \( \sigma \)). The exact details
of these derivations will not be presented here, but can be found in most solid state physics texts (Ashcroft and Mermin 1976; Chen 2005).

Consider the flux of charge carriers through a plane perpendicular to an applied electric field with no temperature gradient present. Electrons will be considered here, though a similar treatment can be done for holes. The net current density $J_e$ is obtained by integrating over all possible directions above and below the plane in k-space (Chen 2005)

$$J_e = -\frac{2}{(2\pi^3)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e v x f dk_x dk_y dk_z$$

(2.14)

where $e$ is the electron charge, $v_x$ is the velocity of the electron in the direction of the applied field, and $f$ is the non-equilibrium distribution function obtained by solving the BTE. For the solution found using the RTA (Equation 2.13), the applied electric potential $V$ appears through the force term $F = -e\xi = e\partial V / \partial x$ where $\xi$ is the applied electric field. The non-equilibrium distribution becomes (Chen 2005)

$$f(\vec{r}, \vec{k}, t) = f_0(E) + \tau \left( v_x \frac{\partial f_0(E)}{\partial E} \frac{\partial E_F}{\partial x} + \frac{e\xi}{m} \frac{\partial f_0(E)}{\partial E} \frac{\partial E}{\partial v_x} \right)$$

(2.15)

where $m$ is the carrier mass. This simplifies further to (Chen 2005)

$$f(\vec{r}, \vec{k}, t) = f_0(E) + \tau v_x \left( \frac{\partial E_F}{\partial x} + e\xi \right) \frac{\partial f_0(E)}{\partial E}.$$  (2.16)

The k-space triple integration in Equation 2.14 is transformed into spherical coordinates to allow for integration over the solid angle $d\Omega$. Substituting Equation 2.16 into the transformed version of Equation 2.14 gives (Chen 2005)
\[ J_e = \frac{e^2}{3} \frac{d\Phi}{dx} \int_0^\infty \tau v^2 D(E) \frac{\partial f_0(E)}{\partial E} dE \]  \hspace{1cm} (2.17)

where \( D(E) \) is the electron density of states, \( v \) is carrier velocity, and \( \Phi = V - E_x / e \) is the electrochemical potential. The expression for \( D(E) \) depends on the number of dimensions for which quantum confinement occurs, i.e. whether the transport is 1D, 2D, or 3D in nature. The electron electrical conductivity \( \sigma_e \) is defined by \( J_e = \sigma_e \xi \) such that, using Equation 2.17 (Chen 2005)

\[ \sigma_e = -\frac{e^2}{3} \int_0^\infty \tau v^2 D(E) \frac{\partial f_0(E)}{\partial E} dE. \]  \hspace{1cm} (2.18)

If the carrier velocity \( v \) is converted to \( E \) using \( E = mv^2 / 2 \) for clarity, Equation 2.18 becomes

\[ \sigma_e = -\frac{2e^2}{3m} \int_0^\infty \tau ED(E) \frac{\partial f_0(E)}{\partial E} dE = ne \mu_e \]  \hspace{1cm} (2.19)

where \( n \) is the electron carrier concentration and \( \mu_e \) is the electron mobility (Ashcroft and Mermin 1976; Chen 2005). This is the electrical conductivity for electrons in the system, \( \sigma_e \). For highly n-type doped samples \( \sigma \approx \sigma_e \). A similar expression exists for charge transport by holes. Size effects may enter into Equation 2.19 either through the form of the density of states \( D(E) \) or through boundary scattering effects on the relaxation time \( \tau \).

The expression for the Seebeck coefficient is found in a similar way. Consider the flux of charge carriers through a plane perpendicular to a temperature gradient and an electrical potential difference. Electrons will be considered here, though a similar treatment can be done for holes. Under both an electrical potential difference and
temperature gradient, the perturbed distribution from Equation 2.13 becomes (Chen 2005)

\[
f(\vec{r}, E, t) = f_0(E) + \tau_x \left( \frac{\partial E_F}{\partial x} + \frac{E - E_F}{T} \frac{dT}{dx} + e \xi \right) \frac{\partial f_0(E)}{\partial E}
\]

(2.20)

and the resulting flux of charge carriers is (Chen 2005)

\[
J_e = -\frac{e}{3} \int_0^\infty \xi \tau^2 \left( \frac{\partial E_F}{\partial x} + \frac{E - E_F}{T} \frac{dT}{dx} + e \xi \right) D(E) \frac{\partial f_0(E)}{\partial E} dE.
\]

(2.21)

The charge carrier flux in Equation 2.21 can be rewritten in terms of the electrochemical potential and temperature gradients as (Chen 2005)

\[
J_e = L_{11} \left( -\frac{d\Phi}{dx} \right) + L_{12} \left( -\frac{dT}{dx} \right)
\]

(2.22)

where \( L_{11} \) is simply the electrical conductivity given by Equation 2.19 and \( L_{12} \) is given by (Chen 2005)

\[
L_{12} = \frac{2e}{3mT} \int_0^\infty \xi \tau^2 \left( E - E_F \right) \frac{\partial f_0(E)}{\partial E} D(E) dE.
\]

(2.23)

The Seebeck coefficient \( S \) is defined under open circuit conditions, i.e. \( J_e = 0 \) (Ashcroft and Mermin 1976). Setting Equation 2.22 equal to zero and solving for the ratio of the electrochemical potential gradient to the temperature gradient gives (Ashcroft and Mermin 1976; Nolas, Sharp et al. 2001; Chen 2005)

\[
S_e = \frac{-d\Phi}{dx} \frac{L_{12}}{L_{11}} = \frac{1}{eT} \int_0^\infty \xi \tau E \left( E - E_F \right) \frac{\partial f_0(E)}{\partial E} D(E) dE.
\]

(2.24)
This is the Seebeck coefficient for electrons in the system, $S_e$. For highly n-type doped samples $S \approx S_e$. Contributions from electrons ($S_e$) and holes ($S_h$) to the overall Seebeck coefficient $S$ will be combined into a single expression for $S$ later in this work when two-carrier transport is discussed. Size effects may enter into Equation 2.24 either through the form of the density of states $D(E)$ or through boundary scattering effects on the relaxation time $\tau$. However, due to the presence of $\tau$ in both the numerator and denominator, only changes in the $E$-dependence of $\tau$ affect $S$. As can be seen in Equation 2.24, the Seebeck coefficient is primarily a function of $E_F$. Thus, modeling of Seebeck coefficient measurements offers a powerful method to probe $E_F$ which, in turn, gives the majority carrier type and concentration. When knowledge of the carrier concentration is combined with measured electrical conductivity data, the carrier mobility in the sample can be obtained. This is especially important for nanowires as direct experimental determination of mobility is often difficult or impossible due to their size and 1D geometric configuration. When combined, the obtained information regarding carrier concentration and mobility can help understand small scale energy transport measurement results and guide future research for improved performance. Thus, extraction of important transport characteristics from measured thermoelectric transport property data represents a new, versatile, and important tool in the investigation of nanoscale energy transport.

To illustrate the use and versatility of these analytical methods, examples of their application to the measurement data of InSb, CrSi$_2$, and Bi$_2$Te$_3$ nanowires are presented.
Indium Antimonide Nanowires

Indium antimonide (InSb) is a III-V compound semiconductor widely used in optical detectors, high-speed electronic devices, and magnetic field sensors in part due to its small bandgap (~0.17eV at room temperature (Goldbery 1996)). It also possesses a small effective mass \((0.014m_0\text{, where } m_0 \text{ is the electron rest mass})\) and high carrier mobility \((\sim 77,000 \text{ cm}^2/\text{Vs at } 300 \text{ K})\) compared to other semiconductors (Madelung 2004). Bulk single crystal InSb has been shown to have potential for thermoelectric power generation with a \(ZT\) of 0.6 at 673 K (Yamaguchi, Matsumoto et al. 2005). Additionally, a single band theoretical model by Mingo (Mingo 2004; Mingo 2006) predicted a \(ZT\) greater than 1 at room temperature for InSb nanowires with a diameter below 15 nm. In light of these factors, InSb nanowires are desirable for studying low-dimensional transport and for thermoelectric applications.

In experiments led by Dr. Jae Hun Seol, the Seebeck coefficient and electrical conductivity of an individual InSb nanowire were measured using a substrate-based device fabricated using electron beam lithography. Full experimental details may be found elsewhere (Seol, Moore et al. 2007). The nanowire was obtained from samples grown by collaborators at NASA Ames Research Center using a self-catalyzed vapor-liquid-solid method at ambient pressure (Ye, Yamada et al. 2006). Figure 2.1 shows the measured Seebeck coefficient of the 42 nm diameter InSb nanowire. These values are approximately an order of magnitude smaller than the bulk values reported in literature for doping concentrations of \(2 \times 10^{14}\) and \(7 \times 10^{15} \text{ cm}^{-3}\), respectively (Frederikse and Mielczarek 1955; Yamaguchi, Matsumoto et al. 2005). Figure 2.2 shows the nanowire’s four-probe electrical conductivity which was 33-125% greater (depending on
temperature) than the bulk values reported in the literature for a doping concentration of \(1.7 \times 10^{16}\) and demonstrated a much weaker temperature dependence than seen in bulk (Tanenbaum and Maita 1953).

Figure 2.1: Measured Seebeck coefficient of the InSb nanowire. Calculation results based on the 1D MB (black line) and 3D (grey line) density of states are also shown. Reproduced with permission from J. Seol, A. Moore, S. Saha, F. Zhou, L. Shi, Q. Ye, R. Scheffler, N. Mingo, and T. Yamada, *J. of Applied Physics* 101, 2007, 023706, copyright 2007 American Institute of Physics.

In order to gain a better understanding of the observed electrical conductivity and Seebeck coefficient of the InSb nanowire, theoretical models of these transport coefficients based on the BTE as described above were used by the author (Arden Moore) to analyze the measured results. Only carriers at the \(\Gamma\) valley of the band structure were
considered due to the band gaps at the L and X valleys being much greater than at the Γ valley. In addition, the ratio of electron mobility to hole mobility is approximately 100 for n-type InSb (Jung, Park et al. 1991). As will be shown, the electron concentration in the InSb nanowire was found to be several orders of magnitudes larger than the hole concentration. With these considerations, hole contributions to the electrical conductivity and Seebeck coefficient were ignored such that \( S \approx S_e \) from Equation 2.24 and \( \sigma \approx \sigma_e \) from Equation 2.19. For the Seebeck coefficient expression, the mean free time is assumed to depend on the electron energy according to \( \tau = \tau_0 E^{r_e} \), where \( \tau_0 \) and \( r_e \) are two constants. Appearing in the numerator and denominator, \( \tau_0 \) cancels out and does not affect the solution.

Figure 2.2: Measured electrical conductivity (filled circles) of the InSb nanowire. The black line and the grey line are the calculation results from the 1D MB and 3D models,

For this particular InSb nanowire, \( \tau_e \) was found to be predominantly limited by the boundary scattering mean free time \( \tau_{\text{boundary}} = l_B/v \), where \( l_B \) is the boundary scattering mean free path. The electron velocity \( v \) is proportional to \( E^{1/2} \), giving a \( r_e \) value of -0.5 for a boundary scattering dominated system. Thus for this nanowire’s analysis \( r_e = -0.5 \) was used.

Considering the small effective mass for InSb and the diameter of this sample, there is a potential for confinement-induced quantum size effects such that a 3D density of states cannot be safely assumed. In addition, if quantum confinement does occur the separation between adjacent energy subbands could be comparable to or smaller than the thermal broadening \( (k_BT) \) of the Fermi-Dirac function near room temperature. Hence, the density of states in Equation 2.25 which accounts for multiple 1D subbands is more accurate than a single 1D subband model used by others (Lin, Sun et al. 2000) for calculating the electron transport properties of a 1D system.

\[
D(E)_{1D} dE = \frac{4}{\pi^2 d^2} \left( \frac{2m^*_e}{\hbar^2} \right)^{1/2} \sum_i \left( \frac{n_i H(E - E_i)}{(E - E_i)^{1/2}} \right) dE
\]  

(2.25)

Here, \( d \) is the diameter of the nanowire, \( m^*_e \) is the electron effective mass, the degeneracy factor \( n_i \) equals 1 for \( i = 1, 3, \) and 7 and equals 2 for other \( i \) values in the range between 2 and 10, \( H(E - E_i) \) is the Heaviside function and takes the value of zero and one when \( E \)
is less and greater than $E_i$, respectively, and $E_i = M_i \left( \frac{\pi^2 \hbar^2}{2m_e^*d^2} \right)$ with $M_i = 2, 5, 8, 10, 13, 17, 18, 20, 25,$ and $26$, respectively, for $i = 1, 2 \ldots 10$.

For the measured Seebeck coefficient values shown in Figure 2.1, the Fermi level $E_F$ in Equation 2.24 was adjusted in order to match the data at each temperature. The obtained $E_F$ at each temperature was then used to determine the electron carrier concentration $n$ at different temperatures according to

$$n = \int_0^\infty D(E) f_0(E) dE$$

(2.26)

where $D(E)$ is either the 1D or 3D density of states as appropriate and $f_0(E)$ is the Fermi-Dirac distribution as given in Equation 2.1.

Using the carrier concentration obtained from Equation 2.26, the temperature-dependent electrical conductivity was calculated from $\sigma = ne\mu_e$ (Equation 2.19) where $\mu_e$ is the temperature dependent effective electron mobility. Matthiessen’s rule (Chen 2005) was used to obtain $\mu_e^{-1} = \mu_{\text{bulk}}^{-1} + \mu_{\text{boundary}}^{-1}$, where $\mu_{\text{bulk}}$ and $\mu_{\text{boundary}}$ are the electron mobility for bulk InSb crystals and the mobility associated with boundary scattering in the nanowire, respectively. The bulk mobility is taken from electron mobility data in the literature for single-crystal InSb of varying doping concentrations ranging from very pure to degenerately doped (Putley 1959). The bulk mobility term accounts for both electron-phonon and impurity scattering within the nanowire. For modeling of the nanowire, the electron mean free path due to boundary scattering $l_B$, which was assumed to be a constant value, was adjusted in order to obtain the $\mu_{\text{boundary}} = e l_B / m_e^* v$ which provided the best fit to the experimental electrical conductivity data.
In addition to the 1D multi-subband (MB) density of states in Equation 2.25, the same calculation procedure described above was followed using a 3D density of states in order to fully account for both possible transport regimes. For the 3D density of states, the equations for Seebeck coefficient and carrier concentration are reduced to

\[ S_{3D} = \frac{k_B}{e} \left( \eta - \frac{(r_e + \frac{5}{2})F_{r_e + \frac{3}{2}}}{(r_e + \frac{3}{2})F_{r_e + \frac{1}{2}}} \right); \eta = \frac{E_F}{k_B T}, \quad (2.27) \]

and

\[ n_{3D} = \frac{(2m^* k_B T)^{1/2}}{2\pi^2 h^3} F_{1/2}(\eta), \quad (2.28) \]

where \( F_m(\eta) = \int_0^\infty \frac{\xi^m d\xi}{e^{(\xi - \eta)} + 1} \) is known as the Fermi-Dirac integral of order \( m \) with \( \xi = E / k_B T \). For the single electron band model presented here, all energies are measured relative to the conduction band edge.

For a 1D system, sharp peaks exist in the density of states at the sub band edges which are not observed in a 3D system. Due to these multiple sharp peaks in the 1D MB density of states used here, the determination of \( E_F \) to match the measured Seebeck coefficient data was not as straightforward as for the 3D model. For Fermi levels near one of these peaks, a small change in the energy can result in a large change in the Seebeck coefficient (Kearney and Butcher 1986). As shown in Figure 2.3, this results in a modulation of the Seebeck coefficient when plotted versus Fermi energy as each sub band edge is passed.
Figure 2.3: Calculated Seebeck coefficient versus Fermi level for the 1D MB density of states at different temperatures. Thermal smearing reduces the amplitude of the modulations with increasing temperature. Reproduced with permission from J. Seol, A. Moore, S. Saha, F. Zhou, L. Shi, Q. Ye, R. Scheffler, N. Mingo, and T. Yamada, J. of Applied Physics 101, 2007, 023706, copyright 2007 American Institute of Physics.

The modulation becomes less significant with increasing temperature due to thermal broadening of the Fermi-Dirac distribution, thereby reducing the influence of the sharp peaks in the density of states on the Seebeck coefficient. Below 250 K, the modulation yields multiple possible values of $E_F$ for each of the measured Seebeck coefficient values. However, one may eliminate the majority of the possible solutions at each temperature and obtain a reasonable $E_F$ versus temperature trend via comparison with the measured electrical conductivity trend. This is accomplished by first using the Seebeck data to identify all possibly valid values of $E_F$ at each measured temperature. From these values
the carrier concentration and electrical conductivity that correspond to each possible $E_F$ value are calculated and compared with the measured electrical conductivity.

![Figure 2.4](image)

Figure 2.4: Possible values of $E_F$ (solid black circles) found using the 1D MB model that can yield the measured $S$ at each measured temperature. Fermi level ($E_F$) values used for the 1D MB (black line) and 3D (grey line) models are also shown. Reproduced with permission from J. Seol, A. Moore, S. Saha, F. Zhou, L. Shi, Q. Ye, R. Scheffler, N. Mingo, and T. Yamada, *J. of Applied Physics* **101**, 2007, 023706, copyright 2007 American Institute of Physics.

Through this process the majority of possible $E_F$ values were eliminated and a reasonable trend of $E_F$ versus temperature was obtained. Figure 2.4 shows all possible values of $E_F$ at the measured temperatures as found using the 1D MB model, with the
values of $E_F$ used in the models indicated by the trend lines. The calculated Seebeck coefficient based on the $E_F$ values is shown in Figure 2.1 together with the measurement results, while a similarly plotted comparison with the measured electrical conductivity data is shown in Figure 2.2. The 1D MB model demonstrates superior agreement with the measured temperature dependence of the electrical conductivity, suggesting that the transport within the nanowire is 1D in nature.

The $E_F$ values found via the 1D MB model which were able to best match the data as shown in Figure 2.4 lie in the seventh and eighth electron subbands. In addition, the Fermi level usually decreases with increasing temperature in nondegenerate n-type semiconductors. The high $E_F$ values and weakly increasing $E_F$ with temperature trend suggest that the nanowire sample was degenerately doped. Similarly, the carrier concentrations calculated based on the $E_F$ values as shown in Figure 2.5 are orders of magnitude greater than the intrinsic carrier concentration of $2 \times 10^{16}$ cm$^{-3}$ observed in bulk InSb at 300 K (Madelung 2004). A highly degenerate sample is also suggested by the weak temperature dependence of the carrier concentration. Although the nanowire could have been doped from the InSb powders (rated at 99.999% purity) with possibly Te, a known shallow donor for InSb with 0.6 meV ionization energy (Littler and Seiler 1986), more will be said as to a likely doping mechanism in a later section.

Figure 2.6 shows the bulk mobility from literature (Putley 1959) for an electron concentration of $1.15 \times 10^{18}$ cm$^{-3}$, very similar to that found for the nanowire. The mobilities used in the two models for fitting the measured electrical conductivity of the nanowire are shown as well. The difference between bulk and nanowire mobilities arises
from the additional boundary scattering term mentioned previously, with the boundary scattering mean free path serving as an adjustable fitting parameter.

Figure 2.5: Calculated carrier concentrations as a function of temperature for the 1D MB (black line) and 3D (grey line) models. Reproduced with permission from J. Seol, A. Moore, S. Saha, F. Zhou, L. Shi, Q. Ye, R. Scheffler, N. Mingo, and T. Yamada, *J. of Applied Physics* **101**, 2007, 023706, copyright 2007 American Institute of Physics.

As shown in Figure 2.2, the electrical conductivity calculated using the 1D MB density of states shows better agreement with the measurement results than the model utilizing a 3D density of states. From the 3D and 1D MB models, the boundary scattering mean free path $l_B$ was determined to be 52 and 53 nm, respectively, comparable to the measured nanowire diameter of 42 nm. In comparison, the bulk
scattering mean free path of electrons due to electron-phonon and impurity scattering was found to be 468 nm and 485 nm at 300 K using either the 3D or 1D MB model Fermi levels, respectively. Hence, electron transport was dominated by surface scattering which supports the use of $r_z = -0.5$ initially.

Figure 2.6: Electron mobility as a function of temperature. The dashed line is the bulk mobility reported from literature (Putley 1959) for an electron carrier concentration of $1.15 \times 10^{18}$ cm$^{-3}$. The grey and black solid lines are the electron mobilities used to fit the nanowire experimental data with the 3D and 1D MB models, respectively. Reproduced with permission from J. Seol, A. Moore, S. Saha, F. Zhou, L. Shi, Q. Ye, R. Scheffler, N. Mingo, and T. Yamada, *J. of Applied Physics* **101**, 2007, 023706, copyright 2007 American Institute of Physics.
Further information about the carrier dynamics within the sample can by obtained by using a simple, phenomenological, unscreened surface roughness scattering model. Following this approach, an estimate of the nanowire surface specularity ($p$) can be made that depends on root mean square surface roughness ($r_{rms}$) and the electron wavelength ($\lambda_e$) of the incident particles according to $p(\lambda_e) \approx \exp(-16\pi^3 r_{rms}^2 / \lambda_e^2)$ (Ziman 1962).

Physically, the parameter $p$ represents the probability of an incident carrier being scattered from the surface specularly such that the completely specular and completely diffuse surface limits correspond to $p$ values of 1 and 0, respectively. The surface roughness of similar nanowires was found to be in the range of 0.5 - 1 nm by transmission electron microscopy (TEM). The Fermi wavelength $\lambda_F$ is estimated to be $\lambda_F = 2\pi h / \sqrt{2m_e^*E_F} \sim 20$ nm at 300 K based on the Fermi level determined for the 1D MB and 3D models, respectively. This is comparable to the nanowire diameter of 42 nm, offering further support to the 1D energy transport case. Using $\lambda_c = \lambda_F$, the obtained $p$ values range from of 0.26 - 0.72 and 0.29 - 0.73 for the 1D MB and 3D models, respectively. A constant effective mass was used in the above calculations.

These results have major implications regarding the viability of InSb nanostructures for thermoelectric applications. While the low Seebeck coefficient may be able to be remedied with greater impurity control, the non-specular boundary scattering of electrons can severely limit the mobility and electrical conductivity compared to bulk. This result suggests that high $ZT$ predictions from models using the common assumption of specular electron transport may be over predicting the thermoelectric power factor in realistic nanowires with surface roughness of ~0.5 nm.

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While the above analysis was able to provide information on the carrier concentration, mobility, surface specularity, and 1D nature of electron transport within the nanowire, there are a few important points to consider regarding its accuracy. First, many of the material properties used in the analysis such as the electron effective mass and mobility of doped InSb were taken from bulk values in the literature. These parameters in nanowires may differ from what is found in bulk InSb. In addition, the actual diameter for electron transport should be smaller than the outer diameter measured by scanning electron microscopy (SEM) due to the presence of a native oxide layer of undetermined thickness, although the oxide thickness of similar wires from the same growth batch may be observed via TEM and used as a representative value. The analysis does not consider the effects of surface depletion arising from trapped charge states (Bardeen 1947; Kimukin, Islam et al. 2006). It also ignores the possibility of Luttinger liquid-like behavior from strong electron-electron interactions (Zaitsev-Zotov, Kumzerov et al. 2000; Zhou, Seol et al. 2006).

In the preceding analysis, the Fermi level was extracted based on the measured Seebeck coefficient where a preliminary assumption of the $r_e$ value was deemed justifiable due to the small nanowire size. There was initial ambiguity as to whether transport was 1D or 3D in nature, necessitating a comparison of both models with the measured electrical conductivity in order to ascertain which regime best explained the measurement data. In this way, it was required that the electrical conductivity was fit over the measured temperature range rather than used as a means of directly extracting the carrier mobility at each measured temperature. This approach was greatly modified and improved for a later work involving the analysis of larger diameter InSb nanowires.
Following the measurement and analysis of the 42 nm InSb nanowire sample, it was theorized that growth of the nanowires at ambient pressure may have led to the inclusion of oxygen within the nanowires to act as an n-type dopant, degenerately doping the nanowire and degrading the Seebeck coefficient. A growth setup was constructed to facilitate InSb nanowire growth at ambient (760 Torr), low vacuum (~10⁻³ Torr), and high vacuum (~10⁻⁶ Torr) levels to investigate the effect of the base pressure during growth on the doping concentration and resulting thermoelectric properties. High purity InSb powder (99.999% from Alfa Aesar) was used as the source material. The growth and subsequent experimental work were led by Dr. Feng Zhou with full details available elsewhere (Zhou, Moore et al. 2010). The thermal conductivity, Seebeck coefficient, and electrical conductivity of nanowires from these varying growth pressures were measured using a suspended microdevice (Shi, Li et al. 2003; Mavrokefalos, Pettes et al. 2007; Zhou, Szczech et al. 2007), the design and measurement procedure of which will be discussed in greater detail in later chapters. The crystal structure and growth direction of the measured nanowire samples were established by TEM via a through-substrate hole beneath the device, providing more detailed sample information regarding crystal quality and oxide thickness than was available in the previous InSb nanowire work. Following measurement of the thermoelectric transport properties and TEM analysis, transport models were developed by the author (Arden Moore) to study the measured data in order to examine any influence the growth base pressure may have had on the doping concentration. As will be shown, the measurement and analysis results suggest that at higher growth base pressures the nanowires are more Sb-rich than those grown at low pressure, greatly affecting the doping level and transport properties. The measured
thermal conductivity values are not discussed here. Plots of the measured thermal conductivity can be found elsewhere (Zhou, Moore et al. 2010).

Table I. The diameters ($d$), growth base pressures, extracted scattering parameters ($r_e$), carrier concentration ($n$), mobility ($\mu$), and neutral dopant concentration ($N_n$) of the InSb nanowire samples. The bulk mobility ($\mu_{\text{bulk}}$) at the given carrier concentration and $\mu_{\text{ref}}$ calculated using diffuse surface scattering ($p_e=0$) in addition to the bulk impurity and phonon scattering rates are also shown. Values outside (inside) parentheses refer to the case that additional reduction in mobility is caused by neutral impurity (point defect) scattering. The extracted data for NW 4 is for a temperature of 350 K. All other data are for 300 K. Vac = vacuum. N/A = not available.

<table>
<thead>
<tr>
<th>NW label</th>
<th>d (nm)</th>
<th>Base pressure</th>
<th>$r_e$</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$N_n$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
<th>$\mu_{\text{bulk}}(n)$ (cm$^2$/Vs)</th>
<th>$\mu_{\text{ref}}$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seol</td>
<td>42</td>
<td>Ambient</td>
<td>-0.161(-0.492)</td>
<td>8.1(5.4) x 10$^{18}$</td>
<td>8.1 x 10$^{16}$</td>
<td>284(428)</td>
<td>9969(12663)</td>
<td>851(992)</td>
</tr>
<tr>
<td>NW 1</td>
<td>133</td>
<td>Ambient</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>NW 2</td>
<td>144</td>
<td>Low Vac</td>
<td>-0.035(-0.494)</td>
<td>6.4(3.8) x 10$^{18}$</td>
<td>2.1 x 10$^{17}$</td>
<td>177(299)</td>
<td>11590(20716)</td>
<td>2301(3161)</td>
</tr>
<tr>
<td>NW 3</td>
<td>177</td>
<td>High Vac</td>
<td>-0.069(-0.479)</td>
<td>8.5(5.5) x 10$^{17}$</td>
<td>2.2 x 10$^{16}$</td>
<td>941(1449)</td>
<td>29861(33487)</td>
<td>5679(6484)</td>
</tr>
<tr>
<td>NW 4</td>
<td>171</td>
<td>High Vac</td>
<td>-0.131(-0.460)</td>
<td>5.9(4.2) x 10$^{17}$</td>
<td>7.1 x 10$^{15}$</td>
<td>1955(2764)</td>
<td>31873(38119)</td>
<td>6140(7058)</td>
</tr>
</tbody>
</table>

Table I summarizes the diameters and growth conditions for the four InSb nanowire samples presently of interest (labeled at NWs 1-4) as well as the InSb nanowire sample discussed previously. NW 1 and the 42 nm sample analyzed previously were grown at ambient base pressure (Ye, Yamada et al. 2006). NW 2 was grown at low vacuum, while NW 3 and NW 4 were grown at the high vacuum level. As listed, the
diameters of NWs 1-4 are all much larger than the previously measured 42 nm diameter sample.

Figure 2.7: Seebeck coefficient for five InSb nanowires. Also shown are bulk InSb values reported by Yamaguchi et al. and Bowers et al. (Bowers, Ure et al. 1959; Yamaguchi, Matsumoto et al. 2005). Reproduced with permission from F. Zhou, A. L. Moore, M. T. Pettes, Y. Lee, J. H. Seol, Q. L. Ye, L. Rabenberg, and L. Shi, J. of Physics D: Applied Physics 43, 2010, 025406, copyright 2010 Institute of Physics.

Figure 2.7 shows the obtained Seebeck coefficients of the four nanowires measured in this work together with the results for the 42 nm sample and data for bulk InSb (Bowers, Ure et al. 1959; Yamaguchi, Matsumoto et al. 2005). The absolute values of $S$ increased with decreasing growth pressure but all remained well below the magnitude observed for bulk InSb (Bowers, Ure et al. 1959; Yamaguchi, Matsumoto et
al. 2005). Figure 2.8 shows the measured nanowire electrical conductivities as well as bulk data from literature (Bowers, Ure et al. 1959; Yamaguchi, Matsumoto et al. 2005). It is from the Seebeck data in Figure 2.7 that the Fermi level extraction was performed as before. However, due to the much larger diameters of NWs 1-4, a 3D density of states could be safely assumed from the outset without having to resort to electrical conductivity fitting as a means of validation. This allows for direct evaluation of the carrier mobility at each temperature using the measured electrical conductivity and the calculated carrier concentration based on the extracted Fermi level.

The proper value of $r_e$ to use for these nanowires, however, was not as straightforward as in the previous study. The larger diameters result in weaker boundary scattering effects such that a simple initial assumption of $r_e=-0.5$ is not necessarily justified. In these ways the analysis for these larger diameters samples differs significantly from that performed for the 42 nm sample.

The measured $S$ and $\sigma$ results showed a general trend of increasing Seebeck coefficient and decreasing electrical conductivity with decreasing growth pressure, suggesting that the dopant concentration (and, hence, the electron concentration) within the nanowires increased with increased growth base pressure. One possible explanation concerns oxidation of the source material prior to nanowire growth. In this scenario, residual oxygen in the growth environment could oxidize the source material to form $\text{In}_2\text{O}_3$, creating In-deficient growth conditions such that the resulting nanowires are Sb-rich with the extra Sb acting as an n-type dopant. The severity of the oxidation would increase with oxygen concentration as dictated by the base pressure. Thus, nanowires from ambient growth would be more heavily Sb-doped than those from vacuum growth.
The measurement results and analysis to follow suggest that even samples grown at high vacuum are still likely doped by excess Sb such that an intentionally In-rich environment may be required to compensate the oxidation effects and achieve stoichiometric samples.

Figure 2.8: Electrical conductivity ($\sigma$) of the measured InSb nanowires. Also shown is bulk InSb data as reported by Yamaguchi et al. (Yamaguchi, Matsumoto et al. 2005) and Bowers et al. (Bowers, Ure et al. 1959). Reproduced with permission from F. Zhou, A. L. Moore, M. T. Pettes, Y. Lee, J. H. Seol, Q. L. Ye, L. Rabenberg, and L. Shi, *J. of Physics D: Applied Physics* **43**, 2010, 025406, copyright 2010 Institute of Physics.

The analytical modeling of these larger nanowires began in a similar manner to that performed for the 42 nm diameter sample. First, the hole contributions to the
transport coefficients were deemed negligible due to the large electron-to-hole mobility ratio in bulk (Jung, Park et al. 1991) and the degenerate n-type doping implied by the small negative Seebeck coefficient values. Due to the large nanowire diameters of these samples, a bulk 3D density of states was assumed such that the Fermi level at each measured temperature was extracted from the Seebeck coefficient measurement data using Equation 2.27. The respective electron wavelength values for the nanowires ranged between 11 and 30 nm as calculated based on the Fermi level and were comparable to that estimated for the 42 nm diameter sample. These values are much smaller than the nanowire diameters, a fact which supports the assumption of 3D transport. For the Fermi level extraction using Equation 2.27, the value of $r_e$ depends on the dominant scattering process. Both boundary scattering and acoustic phonon scattering yield a $r_e$ value of $-0.5$ (Ziman 1962), from which the initial assumption of $r_e=-0.5$ was made for the smaller diameter sample measured previously. This assumption of dominant boundary scattering is less certain for the larger diameter samples currently under consideration. For bulk InSb it has been shown that above room temperature optical phonon scattering is the dominant process with $r_e \approx 0.5$ (Rode 1971). Meanwhile, the ascribed $r_e$ for scattering of electrons by ionized impurities varies between -0.5 and 1.5 depending on the strength and nature of the impurity screening and the energy dependence of the density of states (Lundstrom 2000). Since boundary scattering dominance could not be assumed, a significant degree of impurity scattering was expected, and the value of $r_e$ varied for different types of impurity scattering, the development of a logical means of estimating the proper $r_e$ values for these samples was required.
As a starting point, the scattering parameter $r_{e, \text{bulk}}$ was determined for bulk InSb at different carrier concentrations $n$. This was accomplished using the measured room-temperature Seebeck coefficient data compiled by Rode (Rode 1971) for n-type bulk InSb crystals at varying $n$. At each given $n$ for the bulk crystal, the Fermi level was obtained from the 3D density of states carrier concentration equation (Equation 2.28), with the effective mass $m_e^*$ depending on $n$ according to the InSb literature (Madelung 2004). The obtained $E_F$ at the given $n$ value for the bulk crystals was then used together with the bulk room temperature $S$ at the same $n$ to determine $r_{e, \text{bulk}}$ from Equation 2.27. As shown in Figure 2.9, $r_{e, \text{bulk}}$ decreases from about 0.675 at $n = 5.0 \times 10^{16}$ cm$^{-3}$ to about -0.225 at $n = 1 \times 10^{19}$ cm$^{-3}$ for n-type bulk InSb crystals. This $r_{e, \text{bulk}}$ vs. $n$ relationship can be fit by assigning a scattering parameter $r_{e, \text{ph}} = 0.8$ for electron-phonon scattering and $r_{e, i} = -0.45$ for impurity scattering based on the relation (Goldsmid 1964)

$$r_{e, \text{bulk}}(n) = \left[ \frac{r_{e, \text{ph}}}{\mu_{\text{ph}}} + \frac{r_{e, i}}{\mu_{i, \text{bulk}}(n)} \right] \mu_{\text{bulk}}(n)$$ \hspace{1cm} (2.29)

where $\mu_{\text{bulk}}(n)$ is the mobility found in literature for bulk InSb at carrier concentration $n$ (Rode 1971). The electron-phonon scattering mobility $\mu_{\text{ph}}$ is taken as the $\mu_{\text{bulk}}(n)$ value for the near intrinsic case at $n = 1.67 \times 10^{16}$ cm$^{-3}$, and $\mu_{i, \text{bulk}}(n)$ is the impurity scattering mobility at carrier concentration $n$ obtained using Matthiessen's rule

$$\mu_{\text{bulk}}(n)^{-1} = \mu_{\text{ph}}^{-1} + \mu_{i, \text{bulk}}(n)^{-1}.$$ \hspace{1cm} (2.30)

The impurity scattering parameter $r_{e, i} = -0.45$ obtained in this way for doped bulk InSb crystals is close to the theoretical value of -0.5 for the strongly screened ionized impurity scattering case (Lundstrom 2000).
Figure 2.9: Scattering parameter \((r_{e,\text{bulk}})\) extracted from literature Seebeck coefficient data (Rode 1971) for n-type bulk InSb at varying carrier concentrations \((n)\). The line is the fitting result using \(r_{e,ph} = 0.8\) and \(r_{e,i} = -0.45\). Reproduced with permission from F. Zhou, A. L. Moore, M. T. Pettes, Y. Lee, J. H. Seol, Q. L. Ye, L. Rabenberg, and L. Shi, *J. of Physics D: Applied Physics* **43**, 2010, 025406, copyright 2010 Institute of Physics.

The above analysis is indeed useful, but does not yet account for the influence of boundary scattering or neutral surplus Sb impurities on \(r_e\) for the nanowires under study. The excess Sb atoms within the samples are expected to be ionized in the measurement temperature range due to the small band gap and typically very small activation energy of dopants in InSb. A high electron concentration is then to be expected in the measured nanowires which act to strongly screen the carriers from the ionized impurity centers.
For the case of strong screening $r_{e,i} = -0.5$, which is the same as the value for boundary scattering and point defect scattering in the nanowires (Podor 1983).

Additionally, a small fraction of the excess Sb atoms that are not ionized could lead to neutral impurity scattering for which the scattering parameter $r_{e,n} = 0$ (Lundstrom 2000). Taking into consideration the bulk scattering $r_e$ for high doping, boundary scattering, and the likelihood of neutral and strongly screened impurity scattering, the $r_e$ value for the measured nanowires is expected to lie between -0.5 and 0. Based on this reasoning, the Fermi level extraction from the measured $S$ data using Equation 2.27 was performed with $r_e$ values in the range between -0.5 and 0. The carrier concentration was then calculated for each of the obtained Fermi level values using Equation 2.28. Finally, using these calculated carrier concentrations $n$ along with the measured nanowire electrical conductivity $\sigma$, the electron mobility $\mu$ was determined using $\sigma = n e \mu$ (Equation 2.19). This differs significantly from the analysis of the 42 nm sample where, due to ambiguity as to the 1D or 3D nature of the density of states, the mobility was adjusted to examine the overall fit of the calculated electrical conductivity with the measurement data rather than acting as an extracted value.

As a basis of comparison to the as-obtained nanowire electron mobility $\mu$, a nanowire reference mobility $\mu_{ref}$ is used. This reference mobility represents the expected electron mobility if all scattering rates from electron-phonon and impurity scattering processes within the nanowire are the same as in bulk InSb at the same $n$ with only additional boundary scattering included as a result of the nanowire geometry. This value is obtained using Matthiessen’s rule.
\[ \mu^{-1}_{\text{ref}} = \mu_{\text{bulk}}(n)^{-1} + \mu_{e,B}(n)^{-1} \]  

(2.31)

where \( \mu_{e,B}(n) \) is the boundary scattering mobility calculated by

\[ \mu_{e,B}(n) = \frac{e l_{e,B}}{m_e^* v_e(n)}. \]  

(2.32)

In Equation 2.32, \( v_e \) is the electron velocity that depends on \( n \) and \( l_{e,B} \) is the electron-boundary scattering mean free path that is evaluated according to

\[ l_{e,B} = \frac{1 + p_e d}{1 - p_e} \]  

(2.33)

where \( d \) is the nanowire diameter and \( p_e \) is the specularity parameter in the range between 0 and 1 as described previously (Ziman 1962). Using \( -0.5 \leq r_e \leq 0 \), the obtained mobility \( \mu \) was found to be much smaller than \( \mu_{\text{bulk}}(n) \) and at least three times smaller than the \( \mu_{\text{ref}} \) calculated with \( p_e = 0 \). This is shown in Table I where \( r_e \) for each measured nanowire was calculated based on the procedure discussed below.

The large difference between the extracted nanowire electron mobility \( \mu \) and \( \mu_{\text{ref}} \) suggests that impurity scattering within the nanowires was stronger than typically observed in bulk InSb crystals at the same carrier electron concentration. In the literature on n-type bulk InSb crystals, samples were usually doped with substitutional tellurium (Te) at Sb lattice sites (Madelung 1964). For this doping mechanism, the Te donor atom has one extra valence electron compared to Sb such that the valence difference \( Z \) between the expected atom and the replacement atom is 1. For the proposed nanowire doping mechanism of environment-induced excess Sb, however, a substitutional Sb atom occupies an expected In lattice site. In this situation, Sb has two additional valence
electrons by comparison to In and $Z = 2$. Ionized impurity scattering mobility ($\mu_{i,i}$) is proportional to $N_i^{-1}Z^2$ (Ziman 1962), where $N_i$ is the concentration of the ionized impurities. Thus, for two systems with the same electron concentration $n \approx N_i Z$, $\mu_{i,i}$ is proportional to $Z^{-1}$. It then follows that the ionized impurity scattering mobility $\mu_{i,i}$ for Sb doping ($Z = 2$) in the nanowires would be approximately half of the $\mu_{i,\text{bulk}}(n)$ value found from Equation 2.30 for bulk crystals doped by Te ($Z = 1$) at the same $n$. Additional scattering could also occur from neutral (non-ionized) excess Sb sites. Then for the nanowire case with excess Sb doping and neutral impurities considered, the electron mobility is expressed as

$$\mu(n)^{-1} = \mu_{\text{ph}}^{-1} + 2\mu_{i,\text{bulk}}(n)^{-1} + \mu_{e,B}(n)^{-1} + \mu_{e,n}^{-1}$$

(2.34)

which can be used with the extracted mobility $\mu$ at each data point and other attainable mobilities ($\mu_{\text{ph}}$, $\mu_{i,\text{bulk}}(n)$, and $\mu_{e,B}(n)$ as described previously) to obtain $\mu_{e,n}$, the mobility resulting from scattering by neutral impurities. For the boundary scattering mobility $\mu_{e,b}(n)$, diffuse surface scattering ($p_e = 0$) was assumed due to rather rough nanowire surfaces observed in the TEM images. Using this mobility model, the effective scattering parameter $r_e(n)$ was found for each measured nanowire through iteration of Equations 2.27, 2.28, 2.19, 2.34 and 2.35 until all of the relations were satisfied and self-consistent.

$$r_e(n) = \left[ \frac{r_{\text{ph}}}{\mu_{\text{ph}}} + \frac{2r_{e,i}}{\mu_{i,\text{bulk}}(n)} + \frac{r_{e,b}}{\mu_{e,B}(n)} + \frac{r_{e,n}}{\mu_{e,n}} \right] \mu(n)$$

(2.35)

However, it is also possible that the additional electron scattering was due to point defects besides substitutional impurities. For this case, $r_e = -0.5$ (Podor 1983) and Equation 2.35 is modified to
\[ \mu(n)^{-1} = \mu_{ph}^{-1} + 2\mu_{e,\text{bulk}}(n)^{-1} + \mu_{e,b}(n)^{-1} + \mu_{e,PD}^{-1} \] (2.36)

from which the point defect scattering mobility \( \mu_{e,PD} \) in the nanowire may be obtained in a similar manner to that described for the neutral impurity case previously. The iterative procedure to procure the effective scattering parameter \( r_e(n) \) was then performed until Equations 2.27, 2.28, 2.19, 2.36 and 2.37 were all satisfied and self-consistent

\[ r_e(n) = \left[ \frac{r_{ph}}{\mu_{ph}} + \frac{2r_{e,i}}{\mu_{i,\text{bulk}}(n)} + \frac{r_{e,b}}{\mu_{e,b}(n)} + \frac{r_{e,PD}}{\mu_{e,PD}} \right] \mu(n) \] (2.37)

The results obtained for both the neutral impurity and point defect cases are shown in Table I. In the case of neutral impurity scattering, the neutral impurity concentration \( (N_n) \) was determined to be in the range of \( 7.1 \times 10^{15} \text{ cm}^{-3} \) to \( 2.1 \times 10^{17} \text{ cm}^{-3} \) based on (Seeger 1999)

\[ \mu_{e,n} = \frac{e^3 m_e^*}{80\pi N_n \hbar^3 \varepsilon} \] (2.38)

where \( \varepsilon \) is the dielectric constant of InSb (Madelung 2004). All results were obtained taking into account the \( n \)-dependence of \( m_e^* \). If the dependence of \( m_e^* \) on \( n \) is ignored, the obtained \( \mu \) values for the measured nanowires are still well below \( \mu_{\text{ref}} \). This illustrates that, irrespective of the \( m_e^* \) data used in the analysis, diffuse surface scattering alone is insufficient to suppress the electron mobility to the values found for these large diameter nanowires.

The analyses of both the smaller 42 nm diameter sample and the larger diameter InSb nanowires presented in this section followed the same basic approach of using the measured Seebeck coefficient data to determine the Fermi level, calculating the carrier
concentration based on the extracted Fermi level, and then determining the carrier mobility from the measured electrical conductivity and acquired carrier concentration. This method yields important information which may not be directly obtainable for nanowire samples including the Fermi level, carrier concentration, electron mobility, and, depending on the specific situation, surface specularity, neutral impurity concentration and/or point defect concentration. However, the assumptions and specifics by which the analyses were accomplished differed greatly for the two sets of samples due to the varying diameters and knowledge of the important physical processes involved. Thus, while the general approach is very simple, the implementation can vary in scope and complexity according to material system or situation. In the next section, the analytical modeling of measured CrSi$_2$ nanowire thermoelectric properties is presented for which many of the complications like those observed in InSb are not present. This then serves as a validation of the modeling approach as well as a demonstration of its usefulness towards data analysis and guiding future research.

**Chromium Disilicide Nanowires**

Chromium disilicide (CrSi$_2$) is one of several semiconducting silicides to have been investigated for thermoelectric applications (Rowe 1994; Borisenko 2000), the most promising of which thus far are higher manganese silicide (MnSi$_{1.8}$) with $ZT$ up to 0.7 (Rowe 1994) and rhenium silicide (ReSi$_{1.8}$) with $ZT$ up to 0.8 (Sakamaki, Kuwabara et al. 2003). The peak $ZT$ for both compounds occurs in the intermediate temperature range of 500 – 900 K, making them well-suited for waste heat recovery. The crystal structure of
CrSi$_2$ leads to anisotropic transport properties parallel and perpendicular to the $c$ axis of the unit cell as observed experimentally (Nishida 1972).

In a set of experiments led by Dr. Feng Zhou, the Seebeck coefficient, electrical conductivity, and thermal conductivity of several individual CrSi$_2$ nanowires were measured using the suspended microdevice mentioned previously in the InSb section and which will be covered in detail in later chapters. Upon completion of the measurements, TEM analysis was performed to determine the crystal quality and orientation of the samples. This is especially important when comparing the measured properties to bulk given the known anisotropic nature of bulk CrSi$_2$. Briefly, the diameters were measured by TEM to be 78, 97, and 103 nm for nanowire NW samples NW 1, NW 2 and NW 3, respectively. The growth direction of the nanowires was determined to be along the $<0001>$ (parallel to $c$ axis) direction for all three samples. The nanowires were grown by the Jin group at the University of Wisconsin-Madison. Full experimental details may be found elsewhere (Zhou, Szczech et al. 2007).

Figure 2.10(a) shows the measurement results of Seebeck versus temperature for the three nanowires together with data reported by Nishida (Nishida 1972) for bulk CrSi$_2$ crystals and Shinoda et al. (Shinoda, Asanabe et al. 1964) for several compositions including CrSi$_2$, CrSi$_{2.01}$ and CrSi$_{2.02}$. The anisotropic thermoelectric properties Nishida reported are for directions parallel and perpendicular to the $c$ axis indexed as the $<0001>$ and $<10\overline{1}0>$ directions, respectively. The crystal direction for the reported properties of Shinoda et al. was not specified, although Shinoda et al.’s results for CrSi$_2$ are similar to Nishida’s results along the $<0001>$ direction. The measured thermal conductivity values are not discussed here but may be found elsewhere (Zhou, Szczech et al. 2007).
Figure 2.10: (a) Seebeck coefficient for three CrSi$_2$ nanowires along with bulk data reported by Shinoda et al. (Shinoda, Asanabe et al. 1964) and Nishida (Nishida 1972). The blue, red, and green solid lines in (a) are calculation results from Equation 2.39 using the extracting Fermi energies. (b) Fermi energy of the nanowire and bulk samples. (c) Hole concentration normalized by $p$ at 300 K as a function of 1000/T for the measured nanowire samples. Inset: $p$ for the nanowire samples and bulk. Reproduced with permission from F. Zhou, J. Szczech, M. T. Pettes, A. L. Moore, S. Jin, and L. Shi, *Nano Letters* 7(6), 2007, pp.1649-1654, copyright 2007 American Chemical Society.
As before with the InSb nanowire models, the measured Seebeck coefficient data was used to extract the $E_F$ of the three nanowires at each temperature. In literature, the hole effective mass $m_h^*$ in bulk CrSi$_2$ samples was determined experimentally to be $m_h^* = 5m_0$ (Shinoda, Asanabe et al. 1964; Nishida 1972) where $m_0$ is the electron rest mass. Due to this large effective mass, the energy separation between adjacent hole subbands in the nanowires estimated from $\Delta E \approx 3\left(\pi^2 h^2\right)/2m_h^*d^2$ only becomes comparable to thermal energy at temperatures below 1 K, well below the measured temperature range. Hence, for the temperatures and nanowire diameters studied here there exists little possibility of quantum confinement effects to modify the band structure, density of states, or effective mass. Thus, a bulk 3D density of states was used in the Seebeck coefficient expression which, for holes, simplifies to

$$S_h = \frac{k_B}{e} \left\{ \frac{(r_p + 5/2)F_{r_p,3/2}(\eta)}{(r_p + 3/2)F_{r_p,1/2}(\eta)} - \eta \right\}; \eta = \frac{E_F}{k_BT}$$

(2.39)

where $S_h$ is the hole Seebeck coefficient and $F_r(\eta)$ is the Fermi-Dirac integral

$$F_r(\eta) = \int_0^\infty \frac{\zeta^r}{\exp(\zeta - \eta) + 1} d\zeta .$$

(2.40)

It should be noted that in the conduction band modeling of InSb transport energies were measured relative to the conduction band edge, whereas in this hole transport model the energies are measured relative to the valence band edge. Similar to the electron transport case, the Seebeck coefficient in Equation 2.39 depends on the exponent $r_h$ in the energy dependence of the hole relaxation time $\tau_p$, i.e. $\tau_p = \tau_0 E_p^{r_h}$, where $\tau_0$ and $r_h$ are constants. Also similar to the electron case already described, the parameter $r_h$ takes a value of -0.5
when the mobility is limited by either acoustic phonon scattering (Ziman 1962; Shinoda, Asanabe et al. 1964) or boundary scattering (Seol, Moore et al. 2007). At temperatures above 150 K, acoustic phonon scattering has been shown in literature to be the dominant carrier scattering mechanism in bulk CrSi$_2$ (Shinoda, Asanabe et al. 1964; Nishida 1972). Thus, $r_h = -0.5$ was deemed appropriate for $T > 150$ K and used in the subsequent analysis. For temperatures below 150 K, impurity scattering could become increasingly important so that $r_h$ could deviate from its constant value for high temperatures. Unlike bulk InSb which has been studied extensively in the past, there have been far fewer in depth studies on bulk CrSi$_2$. As a result, the methods employed in the previous section for the large diameter InSb samples which utilized bulk properties at various carrier concentrations to determine the proper scattering exponent for a given nanowire sample are not available for this material. Therefore, $r_h$ cannot be determined accurately for low temperatures and $r_h = -0.5$ was used to analyze only the measurement data for $T > 150$ K. This is also the more relevant temperature range for practical use of metal silicides in thermoelectric applications.

As found by Shinoda et al. (Shinoda, Asanabe et al. 1964), CrSi$_2$ is naturally a highly degenerate p-type semiconductor with hole mobility about 100 times higher than the electron mobility. Hence, although a two band model (electron and hole contributions both considered) was developed initially, the two band model was found to yield the same result as a single valence band model for both the bulk CrSi$_2$ crystals and the nanowires studied here. For simplicity, a single band model only is presented where
$S \approx S_4$ and $\sigma \approx \sigma_h$. Here, $\sigma_h$ is the hole electrical conductivity given by $\sigma_h = p e \mu$ where $p$ is the hole carrier concentration and $\mu$ is the hole mobility.

Following the fundamental approach of the analytical modeling procedure, the Fermi energy $E_F$ was extracted from the measured Seebeck coefficient data at each temperature using Equation 2.39. For comparison, the Fermi level for bulk samples was determined for the literature values in (Nishida 1972) and (Shinoda, Asanabe et al. 1964) using the same Seebeck model. The obtained $E_F$ values are plotted in Figure 2.10(b). The results show that the Fermi levels of both the nanowires and bulk reside well within the valence band, indicating that the CrSi$_2$ nanowires as well as the bulk crystals were degenerate p-type semiconductors, consistent with the findings in literature. The obtained $E_F$ values were then used to calculate the hole concentration at each temperature from

$$p = \frac{(2m^*_h k_B T)^{3/2}}{2\pi^2 \hbar^3} F_{1/2}(\eta) \tag{2.41}$$

Finally, the calculated hole concentration from Equation 2.41 and the measured electrical conductivity were used to obtain the carrier mobility $\mu$ from the relation $\sigma = p e \mu$. This approach to determining the carrier mobility was used in the previous InSb analysis for the large diameter samples, though not the smaller 42 nm sample due to reasons already discussed. In the case of the large diameter InSb nanowires, however, the obtained values of $\mu$ were dependent on how well the scattering exponent was known, leading to different values of $\mu$ for different possible scattering mechanisms. Here, there is little
ambiguity regarding the scattering exponent and the obtained hole mobility $\mu$ is much more certain.

Figure 2.11(a) shows the measured electrical conductivity for the three nanowires while the extracted nanowire carrier mobility values are plotted in Figure 2.11(b). Bulk values are shown in both plots. Unlike the Fermi level comparison for which the same model was applied to bulk measurements as was used for the nanowires, the bulk mobility values in Figure 2.11(b) were measured directly by the original investigators and are taken from the literature (Shinoda, Asanabe et al. 1964; Nishida 1972). The magnitude and temperature dependence of the nanowire mobility values are very similar to the bulk values along the $<0001>$ direction obtained by Nishida (Nishida 1972) and are smaller than those for Shinoda et al.’s samples for which the crystal direction was not specified (Shinoda, Asanabe et al. 1964).

Bulk-like transport in CrSi$_2$ nanowires is to be expected given its large effective mass and naturally low mobility. The low mobility is indicative of a short intrinsic carrier mean free path such that boundary scattering in a nanowire with diameter of tens of nanometers is not likely to greatly reduce the mobility below bulk values. In this way, recover of the bulk mobility serve to help validate both the measurement procedure and the analytical modeling approach. This was not the case for InSb which is known for its extremely high bulk electron mobility (Madelung 2004). For InSb nanowires, the boundary scattering greatly reduced the electron mean free path and compromised the thermoelectric properties. Based on these observations, it seems that materials such as metal silicides for which the bulk mobility is inherently low offer a potential opportunity to observe bulk-like electrical transport in nanostructures which may be combined with
reduced thermal conductivity to realize an enhanced $ZT$. This is the motivation for investigating the higher manganese silicide (HMS) nanostructures discussed in Chapter 5.

Figure 2.11: (a) Electrical conductivity and (b) hole mobility for three CrSi$_2$ nanowires, bulk CrSi$_2$, CrSi$_{2.01}$, and CrSi$_{2.02}$ reported by Shinoda et al. (Shinoda, Asanabe et al. 1964), and bulk crystals in $<0001>$ and $<10\bar{1}0>$ directions reported by Nishida (Nishida 1972). Reproduced with permission from F. Zhou, J. Szczech, M. T. Pettes, A. L. Moore, S. Jin, and L. Shi, Nano Letters 7(6), 2007, pp.1649-1654, copyright 2007 American Chemical Society.
The analysis of CrSi$_2$ nanowires was the least complex for the nanowire systems analyzed thus far. However, even in the more complex cases involving the InSb nanowire the models were first reduced to single band analyses based on the measurement results and known material mobility ratios. In the following section, a two band analysis was required in order to analyze the measurement results for Bi$_2$Te$_3$ nanowires. This further illustrates the flexibility and adaptability of the approach to even multi-carrier systems.

**Bismuth Telluride Nanowires**

For bulk thermoelectrics, bismuth telluride and its alloys with a maximum $ZT$ close to unity have remained the most widely used materials for near room temperature applications. It is then only natural that bismuth telluride should be of interest to investigators searching for high $ZT$ thermoelectric nanostructures. For this reason, bismuth telluride (Bi$_2$Te$_3$) nanowires have received much attention both in terms of synthesis and property measurement. A previous investigation of the thermoelectric transport properties of individual electrodeposited Bi$_2$Te$_3$ nanowires deposited with different Bi to Te ratios in the electrolytes by Zhou et al. (Zhou, Jin et al. 2005) was performed using a suspended microdevice approach similar to that used for the InSb and CrSi$_2$ nanowires already discussed. The measured nanowire properties were quite different from those reported for bulk Bi$_2$Te$_3$ crystals (Fleurial, Gailliard et al. 1988) and showed a marked sensitivity to stoichiometric deviation with both positive and negative Seebeck coefficient values obtained for different samples. However, the measurements were performed on an earlier microdevice design that did not allow for TEM
characterization of the samples, thus leaving detailed knowledge of the crystal quality and structure unknown and preventing any correlation of the measured properties to the crystal properties or chemical composition. Thus, further investigation of the thermoelectric transport properties of individual electrodeposited Bi$_2$Te$_3$ nanowires were required to study of the structure-composition-thermoelectric property relationship and determine if $ZT$ enhancement were possible.

Experiments for this work were led by Dr. Anastassios Mavrokefalos, with full details available elsewhere (Mavrokefalos, Moore et al. 2009). Briefly, the Bi$_2$Te$_3$ nanowires were synthesized by electrodeposition of the constituent materials into the nanopores of anodized alumina templates (Jin, Xiang et al. 2004) with the Bi to Te ratio varied in the electrolyte between different batches of samples. Thermoelectric measurements and TEM analysis were conducted on three individual nanowire samples following a suspended microdevice procedure (Shi, Li et al. 2003; Yu, Saha et al. 2006; Mavrokefalos, Pettes et al. 2007) similar to those used for the large diameter InSb nanowires (Zhou, Moore et al. 2010) and CrSi$_2$ nanowires (Zhou, Szczech et al. 2007) and which will be discussed in more detail later in this work. The TEM analysis of the samples suggests that Sample 3 was single crystalline with few defects or dislocations and had a growth direction along the $<2\bar{1}\bar{1}0>$ perpendicular to the trigonal axis. By contrast, Sample 2 was shown to be polycrystalline with the majority of the nanowire oriented within three degrees of the $<2\bar{1}\bar{1}0>$ direction. Energy dispersive spectrometer (EDS) results of the atomic ratios show a stoichiometry of 43 atomic percentage (at. %) Bi and 57 at % Te for Sample 2, and 74 at. % Bi and 26 at. % Te for
Sample 3 though it should be noted that EDS results of an individual nanowire can contain large errors because of the relatively weak signal. TEM analysis also gave measured nanowire diameters of $55 \pm 1\, \text{nm}$ and $52\, \text{nm} \pm 3\, \text{nm}$ for Sample 2 and 3, respectively. TEM analysis of Sample 1 was not possible due to the sample breaking after measurement. A diameter of $55 \pm 4\, \text{nm}$ was measured for Sample 1 using SEM instead.

Figure 2.12(a) shows the measured Seebeck coefficient versus of temperature, while the measured electrical conductivity is given in Figure 2.12(b). The sample with the highest crystal quality (Sample 3) demonstrated an electrical conductivity more than 3 times higher than polycrystalline Sample 2 or a $6\, \mu\text{m}$ thick electrodeposited polycrystalline film measured in Fleurial et al. (Fleurial, Gailliard et al. 1988). The measured nanowire thermal conductivity is given in Figure 2.12(c). In comparison, the room temperature thermal conductivity for n-type and p-type bulk Bi$_2$Te$_3$ crystals measured by Fleurial et al. varied between 1.8 and 3.3 W/m-K (Fleurial, Gailliard et al. 1988). In the case of the InSb and CrSi$_2$ nanowires, the thermal conductivity was dominated by phonons such that the heat carried by electrons and holes was negligible. For the Bi$_2$Te$_3$ nanowires, this is not necessarily true. A brief analysis of the electronic carrier thermal conductivity for these measurements will be presented shortly which makes use of the carrier dynamics obtained from the analytical methods used to model the Seebeck coefficient and electrical conductivity.
Figure 2.12: Measured (a) Seebeck coefficient, (b) electrical conductivity, and (c) thermal conductivity of Bi$_2$Te$_3$ nanowires. Adapted from images reproduced with permission from A. Mavrokefalos, A. L. Moore, M. T. Pettes, L. Shi, W. Wang, and Z. Li, *J. of Applied Physics* **105**, 2009, 104318, copyright 2009 American Institute of Physics.

Theoretical analysis was performed by the author (Arden Moore) to explain the measurement results and extract the Fermi level, carrier concentration, and carrier mobility. In addition to examining the Seebeck coefficient and electrical conductivity, the Lorenz number for the nanowire samples was also determined using the obtained
Fermi levels and used to calculate the relative contributions of phonons and charge carriers to the measured total thermal conductivity.

There were two possible explanations for the low Seebeck coefficient magnitudes observed for the nanowires in this work as compared to bulk, both of which are depicted in Figure 2.13. The first possibility was that the nanowires were heavily doped, pushing the Fermi level in the nanowires high into the conduction band, resulting in a small Seebeck coefficient and large electrical conductivity due to a large carrier concentration. Under this scenario, the carrier concentrations in the nanowires would be higher than in the bulk samples measured by Fleurial et al. (Fleurial, Gailliard et al. 1988) and electrodeposited thin film measured by Yoo et al. (Yoo, Huang et al. 2005). If this was true, electrical transport could be safely analyzed with a single band model similar to those used in the CrSi₂ nanowire or large diameter InSb nanowire analyses. The second possibility represents the opposite situation where the impurity content was small and the nanowire samples were in the n-p transition region. Near the transition region the electron and hole contributions to the Seebeck coefficient are nearly equal in magnitude but opposite in sign, thus acting to cancel one another out and resulting in a Seebeck coefficient of small magnitude. For this case, nanowire transport would have to be analyzed using a two band transport model which accounts for both carrier types.
Figure 2.13: Example of the determination of the Fermi level from the measured Seebeck coefficient at a given temperature using either the single band or two band model. Reproduced with permission from A. Mavrokefalos, A. L. Moore, M. T. Pettes, L. Shi, W. Wang, and Z. Li, *J. of Applied Physics* 105, 2009, 104318, copyright 2009 American Institute of Physics.

Due to the need to examine both possibilities in order to better understand the distinctly different properties observed in the measured nanowires, a single band model and a two band model were developed and used to analyze the measurement data. Based on the nanowire diameters and the estimated de Broglie wavelength $\lambda_D \approx 9$ nm at room temperature for the growth direction along the binary crystal axis found in Samples 2 and 3, a 3D density of states was deemed appropriate. As before, the mean free scattering times for electrons and holes were assumed to depend on the carrier energy according to
$\tau = \tau_0 E^r$, where $\tau_0$ and $r$ are constants and $r$ can be for either electrons or holes. Based on the bulk mobility temperature dependence (Champness and Kipling 1966), for the measured temperature range the nanowire carrier mobility was expected to be limited by either acoustic phonon scattering or boundary scattering. For both scattering mechanisms, $r$ takes a value of -0.5 (Seol, Moore et al. 2007; Zhou, Szczech et al. 2007). This same value has been used previously for bulk Bi$_2$Te$_3$ studies (Goldsmid 1964) and was found to be appropriate. The total Seebeck coefficient $S$ was calculated as

$$S = \frac{S_e n \mu_e + S_h p \mu_h}{n \mu_e + p \mu_h}$$ (2.42)

where $S_e$ and $S_h$ are the Seebeck coefficients of electrons (Equation 2.27) and holes (Equation 2.39), respectively, $n$ and $p$ are the electron (Equation 2.28) and hole (Equation 2.41) concentrations, respectively, $\mu_e$ is the electron mobility, and $\mu_h$ is the hole mobility (Nolas, Sharp et al. 2001). For clarity, the equations for $S_e$ and $S_h$ are rewritten here in terms of reduced energies to show consistency with the band structure between the two expressions. The electron contribution and hole contribution to $S$ are then written as

$$S_e = -k_B \frac{e}{\mu_e} \left( \frac{(r_e + \frac{5}{2}) F_{r_e + \gamma_e/2}(\zeta_e)}{(r_e + \frac{3}{2}) F_{r_e + \gamma_e/2}(\zeta_e)} - \zeta_e \right)$$ (2.43)

and

$$S_h = k_B \frac{e}{\mu_h} \left( \frac{(r_h + \frac{5}{2}) F_{r_h + \gamma_h/2}(\zeta_h)}{(r_h + \frac{3}{2}) F_{r_h + \gamma_h/2}(\zeta_h)} - \zeta_h \right)$$ (2.44)
where $F_n(\zeta)$ is the Fermi-Dirac integral as already defined and the terms $\zeta_e$ and $\zeta_h$ are the reduced Fermi energies for electrons and holes, respectively. These are related through the band gap by the expressions $\zeta_e = E_F/k_B T$ and $\zeta_h = E_{Fh}/k_B T = -(E_F + E_g)/k_B T$ with $E_F$ and $E_{Fh}$ being the Fermi energies for electrons and holes measured from their respective band edges. The term $E_g$ is the temperature dependant bulk $\text{Bi}_2\text{Te}_3$ bandgap which is given by an empirical relation (Goldsmid 1964). For Sample 3, bulk mobility data (Champness and Kipling 1966) perpendicular to the trigonal direction was used to be consistent with the TEM-determined nanowire growth direction. Bulk mobility data for transport parallel to the trigonal axis could not be found in literature, but was instead approximated following a method used previously in the modeling of $\text{Bi}_2\text{Te}_3$ nanowires. In this approach, the mobility parallel to the trigonal axis is approximated by scaling the bulk mobility values perpendicular to the trigonal axis (Champness and Kipling 1966) by the bulk electrical conductivity anisotropy factors of 4 for electrons and 2.7 for holes (Bejenari and Kantser 2008). For Sample 1 with unknown crystal structure and the polycrystalline Sample 2, the two band analysis was performed for both crystal orientations to encompass all possibilities. The effective mass components used in the analyses are the same as those determined in the work of Bejenari and Kantser, with temperature dependencies of $m_h^* \approx T^{0.17}$ for holes and $m_e^* \approx T^{0.12}$ for electrons (Bejenari and Kantser 2008).

For the two band model where the calculated total Seebeck coefficient is determined by Equation 2.42, it was first assumed that the electron mobility to hole mobility ratio was the same as found in bulk. This allowed the Seebeck coefficient to be determined without any additional variable parameters besides the Fermi level. Using
this approach, $E_F$ was adjusted to match the measured Seebeck coefficient data for each sample in both the transition region and the highly doped region, thereby giving two possible values of the Fermi level for each data point. While both solutions are valid when considering only the Seebeck coefficient data, the carrier concentrations and, as a result, the electrical conductivities associated with each solution are very different. By comparing the measured electrical conductivity values with the magnitudes of the electrical conductivity expected from the two models it was possible to eliminate one of the scenarios and determine the actual case for the nanowire samples.

For the two band model, the electrical conductivity was calculated from

$$\sigma = ne\mu_e + pe\mu_h. \quad (2.45)$$

Since boundary scattering acts to decrease the respective mobilities, the carrier mobilities for the nanowire samples can not be expected to exceed the bulk values. Using these as an upper limit, it was found that even using the bulk mobilities (Champness and Kipling 1966) for several different stoichiometries the electrical conductivity values calculated using Equation 2.45 for $E_F$ in the transition regime were 2-20 times smaller than the measured nanowire conductivities. This result indicates that the observed low Seebeck coefficients were actually the result of high doping levels and that the true Fermi level values should be those of the highly doped regime. As shown in Figure 2.13, for high doping the two band model and the single band model yield the same result. Under these circumstances a single band model of the electron band is sufficient for analyzing the measured transport properties and no initial assumption as to a mobility ratio is required. The single band electron model used in this work closely follows the simple procedure
employed for holes in CrSi$_2$ nanowires (Zhou, Szczech et al. 2007), where Equation 2.43 is used along with the measured Seebeck coefficient data to extract the Fermi level, which allows for $n$ to be calculated from Equation 2.28. This $n$ value is then used in conjunction with the measured electrical conductivity $\sigma$ to obtain the electron mobility $\mu = \frac{\sigma}{ne}$.

![Fermi level as a function of temperature](image)


The Fermi level values obtained from the single band model are shown in Figure 2.14. The corresponding carrier concentrations for the nanowire samples are plotted in Figure 2.15(a) and were found to fall between $6 \times 10^{19}$ cm$^{-3}$ and $1.3 \times 10^{20}$ cm$^{-3}$. The
obtained electron mobility values are shown in Figure 2.15(b). The mobilities from Sample 3 were roughly 2.5 times higher than the mobilities found for Sample 2. This was likely caused by the polycrystalline structure of Sample 2, with grain boundary scattering reducing the mobility beyond that from surface boundary scattering alone. For bulk Bi$_2$Te$_3$ crystals at 300 K, the mobility values from literature are 171 cm$^2$/Vs and 152 cm$^2$/Vs for $n = 5.2 \times 10^{19}$ cm$^{-3}$ and $1.46 \times 10^{20}$ cm$^{-3}$, respectively (Rowe 1994). Extrapolating this trend, the bulk mobility at 300K is estimated to be about 163 cm$^2$/Vs at $n = 1 \times 10^{20}$ cm$^{-3}$, about 19% higher than the obtained mobility values for Sample 3 at similar $n$.

![Figure 2.15](image_url)

Figure 2.15: Calculated (a) electron concentration and (b) mobility for the measured nanowire samples. The two figures share the same legend shown in (a). Adapted from images reproduced with permission from A. Mavrokefalos, A. L. Moore, M. T. Pettes, L. Shi, W. Wang, and Z. Li, *J. of Applied Physics* **105**, 2009, 104318, copyright 2009 American Institute of Physics.
Using the extracted nanowire mobilities in conjunction with bulk mobility values, the surface specularity $p$ was estimated. If it is assumed that $n$ is approximately the same as the ionized impurity concentration, then when comparing nanowire and bulk mobilities with the same $n$ the difference in mobility would be primarily due to additional boundary scattering associated with the nanowire. Using Matthiessen’s rule, the boundary scattering mobility $\mu_{\text{boundary}}$ was obtained using the extracted nanowire mobility $\mu$ and the bulk mobility $\mu_{\text{bulk}}$ from

$$\mu_{\text{boundary}}^{-1} = \mu^{-1} - \mu_{\text{bulk}}^{-1}.$$  \hfill (2.46)

The boundary scattering mean free path $l_b$ is then found from

$$\mu_{\text{boundary}} = \frac{e l_b}{m_{\text{ec}}^* v_F}$$  \hfill (2.47)

where $m_{\text{ec}}^* = 1.27 m_0$ is the electron conductivity effective mass which differs from the density of states effective mass used in carrier concentration calculations (Fleurial, Gailliard et al. 1988) and $v_F$ is the Fermi velocity calculated to be $\sim 5 \times 10^5$ m/s from the Fermi level of Sample 3. From this approach, the boundary scattering mean free path $l_b$ for Sample 3 was found be 112 nm at 300 K. The boundary scattering mean free path is related to the surface specularity and nanowire diameter by Equation 2.33, from which a surface specularity of 0.7 was found. As discussed previously, this nearly-specular scattering of charge carriers from the nanowire boundaries is extremely important information when evaluating the nanowires’ potential for $ZT$ enhancement. By comparison, the bulk electron mean free path $l_{e,\text{bulk}}$ which is primarily limited by phonon
and impurity scattering, was estimated in a similar manner to be 61 nm at room temperature.

To investigate the relative contribution of electrons to the measured total thermal conductivity $\kappa$, the electron contribution $\kappa_e$ to the thermal conductivity of Samples 2 and 3 were calculated using the Wiedemann-Franz law

$$\kappa_e = \sigma T \left( \frac{k_B}{e} \right)^2 L$$

where $L$ is the dimensionless Lorenz number given by

$$L = \frac{e^2}{k_B T^2} \left( \frac{L_{22}}{L_{11}} - T^2 \frac{L_{12}^2}{L_{11}^2} \right).$$

The transport integrals in Equation 2.49 are defined as (Nolas, Sharp et al. 2001; Chen 2005)

$$L_{11} = \sigma = -\frac{2e^2}{3m_e^*} \int_0^\infty \frac{\partial f_0}{\partial E} D(E) E \pi dE,$$

$$L_{12} = S \sigma = \frac{2e}{3m_e^* T} \int_0^\infty \frac{\partial f_0}{\partial E} D(E) E(E - E_F) \pi dE,$$

and

$$L_{22} = -\frac{2}{3m_e^* T} \int_0^\infty \frac{\partial f_0}{\partial E} D(E) E(E - E_F)^2 \pi dE.$$
shows the obtained $\kappa_e$ for Sample 2 and Sample 3 using Equation 2.48, Equation 2.52, and the measured nanowire Seebeck coefficient and electrical conductivity data.

The difference between the measured total thermal conductivity $\kappa$ and the calculated $\kappa_e$ is due to the lattice contribution ($\kappa_l$) and a bi-polar contribution ($\kappa_{e-p}$) (Goldsmid 1956). The model of Gallo et al. (Gallo, Chandrasekhar et al. 1963) was used to calculate $\kappa_{e-p}$ from the extracted $E_F$, $n$, and $\mu$ of electrons. The calculation results show that $\kappa_{e-p}$ is less than 0.01 W/m K for the highly doped nanowires within the measured temperature range. Similarly, the high n-type doping level results in a negligible thermal conductivity contribution from holes. Hence, the phonon thermal conductivity is obtained as $\kappa_{ph} = \kappa - \kappa_e$ at each data point for the nanowire samples. This is plotted in Figure 2.16(b) with error bars originating from the thermal conductivity measurement uncertainty. The phonon thermal conductivity $\kappa_{ph}$ was calculated for bulk and diffuse surface nanowires with the same diameters as Samples 2 and 3 using the phonon thermal conductivity model of Morelli et al. (Morelli, Heremans et al. 2002) and bulk phonon dispersion curve data (Jenkins, Rayne et al. 1972) along the binary axis. Details of this calculation may be found elsewhere (Mavrokefalos, Moore et al. 2009) and are outside the scope of the current discussion. These calculation results are the curves shown in Figure 2.16(b). As a validation check, the calculated bulk thermal conductivity is in agreement with the reported $\kappa_{ph}$ of about 1.5 W/m K for bulk Bi$_2$Te$_3$. 
Figure 2.16: (a) The calculated electron thermal conductivity $\kappa_e$. (b) The obtained phonon thermal conductivity $\kappa_{ph}$. The two figures share the same legend for the measurement data as shown in (a). Curves in (b) are the calculated $\kappa_{ph}$ for bulk and nanowires with the same diameter as Samples 2 and 3 assuming diffuse phonon boundary scattering. Adapted with permission from A. Mavrokefalos, A. L. Moore, M. T. Pettes, L. Shi, W. Wang, and Z. Li, *J. of Applied Physics* **105**, 2009, 104318, copyright 2009 American Institute of Physics.

In this analysis, important information beyond just the carrier concentration and mobility were obtained. First, the true cause of the low Seebeck coefficient magnitudes was determined via analysis of the near-transition and highly doped solutions, with the conclusion of highly doped samples helping to guide researchers on the needed direction regarding improving impurity and stoichiometry control. Secondly, the relatively high surface specularity of 0.7 suggests that Bi$_2$Te$_3$ nanowires may not suffer as great a reduction in mobility due to boundary scattering as seen in the highly doped InSb nanowires. Finally, calculation of the electronic thermal conductivity facilitates the
determination of the phonon thermal conductivity. All of this valuable information was obtained from application of the analytical models to the measured thermoelectric properties and crystallographic analyses, demonstrating how powerful this combination of research methods can be in building an understanding of the relationship between transport coefficients and sample size, quality, and composition.

THERMAL TRANSPORT MODELING USING THE BTE

In the previous section, relations for the Seebeck coefficient and electrical conductivity were derived using the linearized form of the BTE given in Equation 2.13. An expression for the phonon thermal conductivity can be obtained in a similar manner using the equilibrium distribution for phonons (Equation 2.3), although the final form varies according to several factors associated with the exact treatment of the lattice dynamics. A brief, general derivation is presented here while more complicated, specialized models are applied to the modeling of phonon transport in nanowires and graphene.

For phonons passing through a plane perpendicular to an applied temperature gradient, the net heat flux $J_p$ is obtained by integrating over all possible directions above and below the plane in k-space (Chen 2005)

$$J_p = \sum_s \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hbar \omega_{x,s} f dk_x dk_y dk_z \tag{2.53}$$

where $f$ is the non-equilibrium phonon distribution function obtained by solving the BTE. The summation occurs over all the pertinent vibrational polarizations $s$, each of which has its own $\omega-k$ dispersion relation characteristics including the velocity $v_{x,s}$ in the direction

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of the applied temperature gradient. As done previously in the charge carrier treatment, the k-space triple integration in Equation 2.53 is transformed into spherical coordinates to allow for integration over the solid angle \(d\Omega\). Integrating over a hemisphere for 3D transport gives (Chen 2005)

\[
J_q = -\sum_s \frac{1}{3} \int_0^{\omega_{\text{MAX}}} \frac{df_0}{dT} D(\omega) \hbar \omega v_s^2 \tau(\omega) d\omega \frac{dT}{dx}.
\]

(2.54)

where \(D(\omega)\) is the phonon density of states, \(\omega_{\text{MAX}}\) is the maximum phonon frequency, and \(\tau(\omega)\) is the phonon mean free scattering time. This scattering time typically accounts for phonon-phonon, impurity, and boundary scattering processes using simple analytical expressions derived from perturbation theory rather than using the full quantum mechanical approach as mentioned earlier.

Comparing Equation 2.54 to Fourier’s law for phonons \(J_q = -\kappa_{ph} \frac{dT}{dx}\), the phonon thermal conductivity is expressed as (Chen 2005)

\[
\kappa_{ph} = \sum_s \frac{1}{3} \int_0^{\omega_{\text{MAX}}} \frac{df_0}{dT} D(\omega) \hbar \omega v_s^2 \tau(\omega) d\omega.
\]

(2.55)

Equation 2.55 is the general form for the 3D phonon thermal conductivity obtained from the BTE using the relaxation time approximation. However, in practice more complicated formulations which take into account effects of normal phonon-phonon scattering are used. In addition, the details of how the umklapp phonon-phonon scattering is treated vary between different models, as does the selection of the maximum phonon frequency (or frequencies) which serve as the upper limit of integration. The Callaway model (Callaway 1959), for example, uses the Debye frequency as the
integration cutoff, whereas the more complex model developed by Morelli et al. (Morelli, Heremans et al. 2002) has separate cutoffs for each polarization based on the Brillouin zone boundary frequencies. It was the model of Morelli et al. which was used in the analysis of the measured thermal conductivity of the large diameter InSb nanowires and the lattice thermal conductivity of the Bi$_2$Te$_3$ nanowires. Details on both analyses are available elsewhere (Mavrokefalos, Moore et al. 2009; Zhou, Moore et al. 2010) and are not presented here. To date, these RTA-based models have proven to work well for describing 3D phonon transport in bulk solids and nanostructures. In the next section, it is shown how the use of an RTA analytical model fails to accurately describe phonon transport in 2D graphene supported on a substrate.

**SiO$_2$-supported Exfoliated Single Layer Graphene**

Besides being of interest from a fundamental physics point of view, the two-dimensional monatomic sheet of carbon known as graphene has potential for applications in high-speed electronic devices, sensors, memory storage, and spintronics (Geim and Novoselov 2007). In an experiment led by Dr. Jae Hun Seol and described elsewhere (Seol, Jo et al. 2010), the thermal conductivity of single layer exfoliated graphene supported on SiO$_2$ was measured. The measurement results gave a room temperature thermal conductivity of ~600 W/m K, considerably lower than theoretical predictions and early experimental work for the thermal conductivity of suspended graphene monolayers.

To fully understand the results, a RTA-based model for 2D phonon transport in graphene similar to the work of Nika et al. (Nika, Ghosh et al. 2009; Nika, Pokatilov et al. 2009) was developed and used by the author (Arden Moore) and collaborators. In this
model, the phonon thermal conductivity, which dominates any charge carrier thermal conductivity contributions, is expressed as

\[
\kappa_{ph} = \frac{1}{4\pi k_B T^2 t_G} \sum_{s=L,A,T,A,Z} \int_{k_{\text{min},s}}^{k_{\text{max},s}} (\hbar \omega_s(k) v_s)^2 \tau_{\text{tot},s}(k,T) \frac{\exp(\hbar \omega_s(k)/k_B T)}{[\exp(\hbar \omega_s(k)/k_B T) - 1]^2} k dk
\]

(2.56)

where \( t_G = 0.335 \) nm is the graphene thickness, \( k \) is the wavevector, \( k_{\text{max}} \) is the maximum wavevector, the index \( s \) refers to the specific phonon branch, \( k_{\text{min},s} \) is the minimum wavevector for branch \( s \), \( \omega_s(k) \) is the frequency at wavevector \( k \), \( v_s \) is the phonon sound velocity, and \( \tau_{\text{tot},s}(k) \) is the total mean free scattering time. The value of the minimum wavevector \( k_{\text{min},s} \) depends on how interface transmission at the thermal reservoirs on either end of the finite length sample are treated (Seol, Jo et al. 2010). Briefly, for a graphene sample of finite length \( L \), low frequency phonons with mean free path greater than \( L \) do not thermalize locally because of the lack of significant internal scattering. For these low frequency, long mean free path phonons the finite interface transmission coefficient at the contacts determine their thermal conductivity contribution. For zero transmission at the contacts, the lack of interaction with heated phonons means the low frequency phonons would remain at the ambient temperature and thus do not contribute to the net thermal transport. For this case, an appropriate \( k_{\text{min},s} \) would be determined to exclude these phonons with mean free path greater than \( L \) from the thermal conductivity integral. This approach would apply for optical heating where the photonic energy is absorbed by electrons and high-frequency phonons. For perfect transmission at the contacts, ignoring the contribution of low frequency phonons entirely would severely under predict the thermal conductivity for suspended graphene at low temperatures. In addition, it has been predicted that the transmission coefficient at van der Waals contacts
like those used in this experiment increases with decreasing frequency (Prasher 2009). For modeling the perfect transmission case, $k_{\text{min},s} = 0$ and the total mean free scattering time $\tau_{\text{tot},s}(k,T)$ for all phonons is given by

$$
\tau_{\text{tot},s}(k,T) = \tau_{0,s}(k,T) \left( \frac{1}{1 + \frac{l_{0,s}(k,T)}{L}} \right)
$$

(2.57)

where $l_{0,s}(k,T)$ is the phonon mean free path given by $l_{0,s}(k,T) = v_s \tau_{0,s}(k,T)$. Because non-zero transmission is the more likely physical situation for this experiment, this later approach was used for the RTA calculation results shown in Figure 2.17. While the distinction between cases is significant in suspended graphene, it should be noted that the two transmission coefficient limits yield similar results for supported graphene over the measurement range of 80 K to 375 K. This is due to strong substrate scattering of low frequency phonons rendering their thermal conductivity contribution negligible.

Only acoustic phonon branches were considered, namely the longitudinal (LA), transverse (TA), and out-of-plane (ZA) polarizations. As will be discussed, in the RTA formulation the ZA branch has a negligible contribution to the thermal conductivity and can be excluded entirely in Equation 2.56 without affecting the results. The phonon dispersion for suspended graphene calculated by Nika et al. (Nika, Pokatilov et al. 2009) was used, from which $v_s, k_{\text{max}},$ and $\omega_s(k)$ were obtained.

Through the mean free scattering time, scattering of phonons by isotopes, umklapp phonon-phonon processes, and the SiO$_2$ support were accounted for. These separate scattering mechanisms were combined into the total scattering time via
Matthiessen’s rule. For modeling suspended graphene, the SiO$_2$ scattering term was excluded. Isotope scattering by 1.1% C$^{13}$ in the C$^{12}$ crystal as occurs in nature was modeled using a point defect scattering time expression given by Nika et al. (Nika, Pokatilov et al. 2009). The lengthy scattering time expression for the phonon-SiO$_2$ scattering was derived by Dr. Natalio Mingo and can be found in the supplemental materials of Seol et al. (Seol, Jo et al. 2010).

A phenomenological expression (Nika, Ghosh et al. 2009) adapted from an existing graphite model (Klemens and Pedraza 1994) was used to calculate the umklapp phonon-phonon scattering time as

$$\tau_{\mu,s}(k,T) = \frac{1}{\gamma_s^2 k_B T \omega_s(k)^2} \frac{\omega_{s,max}^2}{\omega_{s,max}}$$

(2.58)

where $\gamma_s$ is the Gruneisen parameter, $M$ is the mass of a graphene unit cell, and $\omega_{s,max}$ is the maximum frequency of the respective branch $s$. The graphene Gruneisen parameters calculated by Nika et al. (Nika, Pokatilov et al. 2009) and Mounet and Marzari (Mounet and Marzari 2005) for the LA and TA modes are nearly $k$-independent and were taken to be constant values of $\gamma_{LA} = 1.8$ and $\gamma_{TA} = 0.75$ as done elsewhere in previous works (Nika, Ghosh et al. 2009). Over the majority of $k$-space, the magnitude of the ZA branch Gruneisen parameter is much larger than for either the LA or TA branch, reaching values as low as -80 (Mounet and Marzari 2005). These Gruneisen parameter values, when used in Equation 2.58 for the respective polarizations, produce scattering times for ZA phonons that are orders of magnitude smaller than those of the LA and TA branches. These extremely short scattering times make the contribution of the ZA branch to the thermal conductivity negligible in comparison to those of the LA and TA polarizations.
(Nika, Ghosh et al. 2009). However, Equation 2.58 was derived without rigorously calculating the three-phonon scattering phase space (Klemens and Pedraza 1994). In addition, Equation 2.58 is based on the assumptions of a linear $\omega$-$k$ dispersion relation, long phonon wavelengths, and high temperature. While dispersion relations of the LA and in-plane transverse TA branches are quite linear, the ZA branch has a highly non-linear quadratic dependence of the frequency on the wavevector. Thus, these assumptions lead to the incorrect finding of extremely strong umklapp scattering of ZA phonons, a conclusion that is contradicted by more robust quantum mechanical analysis performed by Dr. Lucas Lindsay and Dr. David Broido at Boston College (Seol, Jo et al. 2010). In their approach, an exact numerical solution to the linearized Boltzmann equation for graphene was obtained without using the RTA. Instead of the RTA, the normal and umklapp three-phonon scattering rates in single layer graphene were determined using full quantum mechanical calculations. These calculations showed that ZA phonons are only allowed to scatter under very strict conditions due to quantum mechanical restrictions, leading to much longer phonon-phonon scattering times than predicted from the RTA expression. This in turn leads to a non-trivial, even dominant contribution to the thermal conductivity by ZA phonons in direct contradiction to the RTA model.

The question as to which physical picture best described thermal transport in graphene was in part answered when both models were used to try and explain the measurement results for the thermal conductivity of the SiO$_2$-supported single layer graphene. The results of both the RTA-based model and the numerical BTE model described previously are shown in Figure 2.17.
Figure 2.17: Measured thermal conductivity of oxide-supported graphene samples G1, G2, and G3 together with the highest reported values of pyrolytic graphite (PG) (Slack 1962). The numerical BTE calculation results for suspended single layer graphene (thick black solid line) and supported single layer graphene with ZA-only substrate scattering (thin blue solid line) or LA-TA-ZA substrate scattering (blue dashed line) are also shown along with the RTA calculation result (thick red dash-dot line) for supported single layer graphene with LA-TA substrate scattering. Reproduced with permission from J. H. Seol, I. Jo, A. L. Moore, L. Lindsay, Z. H. Aitken, M. T. Pettes, X. Li, Z. Yao, R. Huang, D. Broido, N. Mingo, R. S. Ruoff, and L. Shi, Science, in print, 2010, copyright 2010 American Association for the Advancement of Science.
For both models, the strength of the graphene-substrate phonon scattering was adjusted to fit the measured thermal conductivity at 300 K. It was found that the measured thermal conductivity of the SiO$_2$-supported graphene was best explained by the numerical BTE model with strong substrate scattering of the out-of-plane ZA branch and negligible substrate scattering of the in-plane LA and TA branches. The RTA model, for which the ZA branch contribution is predicted to be negligible due to extremely short umklapp scattering times, failed to capture the temperature dependence and magnitudes beyond that fit at 300 K. These combined results suggest that the ZA contribution to the thermal conductivity is indeed large in suspended graphene as predicted by the quantum mechanical scattering analysis and that the measured temperature dependence of the thermal conductivity can be explained by strong (weak) scattering of ZA (LA and TA) phonons by the supporting oxide. Another possible explanation involves indirect substrate-induced enhancement of the umklapp scattering rate for ZA phonons via reflection symmetry breaking (Seol, Jo et al. 2010).

Monte Carlo Simulation of Phonon Transport in Sawtooth Silicon Nanowires

As shown in the previous section, RTA-based analytical solutions to the BTE are not always appropriate or accurate. In other cases, dispersion considerations and geometric complexity can make analytical solution of the BTE intractable even when use of the RTA is acceptable. Through the use of Monte Carlo simulations, however, phonon transport through complex geometries with dispersion characteristics included may be realized. The basic concept is to track the phonon positions, trajectories, and boundary
scattering interactions while simultaneously modeling the phonon populations and interior scattering processes in a manner that is consistent with solid state physics and bulk transport properties. In this way the Monte Carlo simulation solves the BTE indirectly through carrier statistics rather than by using analytical means along with restrictive simplifying assumptions. The fundamentals of how phonons may be modeled in a Monte Carlo framework will not be repeated here, but are readily available in the literature (Mazumder and Majumdar 2001; Chen, Li et al. 2005). Instead, the focus of this section is on the application of Monte Carlo methods to simulate phonon transport through a silicon nanowire with large surface roughness, modeled here as sawtooth facets of varying size and spacing.

Typically in literature, the scattering of incident phonons from a surface is treated as either purely diffuse, purely specular or a combination of both (Ziman 1962). This is expressed by the surface specularity parameter $p$ as described previously and is generally used as a model variable, fitting parameter, or determined sample characteristic for explaining nanostructure measurement results (Mingo 2003; Mingo, Yang et al. 2003; Dames and Chen 2004). For a nanowire of diameter $d$, the effective mean free path ($l_B$) due to surface scattering is related to the surface specularity (Ziman 1962; Dames and Chen 2004)

$$l_B = \frac{1+p}{1-p}d$$ (2.59)

This same equation was used in the modeling of electron transport in Equation 2.33. For surface roughness elements that are random in height but follow a Gaussian
distribution, the specularity parameter $p$ is often estimated from Ziman’s formula (Ziman 1962)

$$p = \exp\left(-16\pi^3 \delta^2 / \lambda^2\right)$$

(2.60)

where $\delta$ is the root mean square surface roughness and $\lambda$ is the phonon wavelength. For very small roughness values such that $\delta$ is several orders of magnitude smaller than the dominant phonon wavelength ($\lambda_0$), $p$ approaches 1 and the surface scattering is highly specular. In this case, because the reflection does not alter the direction or rate of propagation along the gradient, specular surfaces pose no resistance to phonon transport. It then follows that a nanostructure with all specular surfaces would experience no reduction in thermal conductivity from classical size effects and retain its bulk thermal conductivity values. Consider, however, the case of silicon for which the dominant phonon wavelength $\lambda_0 \approx 1$ nm at room temperature (Chen 1997). For such a short wavelength, Ziman’s formula in Equation 2.60 yields a value of $p \approx 0$ when the surface roughness is just 0.3 nm, comparable to atomic surface roughness. According to the above standard treatment, fully diffuse surfaces yield the smallest surface scattering mean free path possible and, hence, the lowest thermal conductivity for a nanowire with randomly distributed surface roughness when the bulk phonon dispersion is still applicable. The thermal conductivity associated with this completely diffuse surfaces case is then referred to as the diffuse surface limit $\kappa_{\text{diffuse}}$. Some nanowire thermal conductivity measurement results found in literature are very close to their respective diffuse limits (Li, Wu et al. 2003; Shi, Hao et al. 2004). However, thermal conductivity values much lower than those given by the diffuse surface limit have been measured for a
22 nm diameter Si nanowire sample grown using a vapor liquid sold (VLS) method with small surface roughness (Li, Wu et al. 2003) as well as arrays of 50 - 70 nm diameter Si nanowires with rough surfaces obtained by electrochemical etching (Hochbaum, Chen et al. 2008). In both cases the nanowire diameters were much larger than $\lambda_0$ for most of the temperature range of the measurement such that the bulk phonon dispersions were still valid and quantum confinement effects were not expected to influence the phonon thermal conductivity.

In an effort to understand these results, Monte Carlo simulations were used to explore whether the surprisingly low thermal conductivity values found in these two Si nanowire studies could have been caused by phonon backscattering from rough surfaces (Moore 2008). A phenomena conceptually similar to this has been reported previously in the form of gas molecules being backscattered in a rough channel (Berman and Maegley 1972). It is theorized that if phonon backscattering of this type were sufficiently strong, thermal conductivity values below the diffuse surface limit could be obtained. Beyond being of interest in terms of studying thermal transport physics, this effect would have implications on thermoelectrics as well where further reduction below the diffuse surface limit could lead to enhancement of $ZT$ in surface-engineered nanostructures.

For simplicity, surface roughness elements were modeled in the form of sawtooth facets with defined height and length rather than attempting to specify and compare random surface morphologies. Besides the nanowires with rough etched surfaces, (Hochbaum, Chen et al. 2008), nanowires with ordered sawtooth surfaces like those explicitly simulated here have also been synthesized (Ross, Tersoff et al. 2005; Johansson, Karlsson et al. 2006; Peng, Meister et al. 2007; Caroff, Dick et al. 2009; Li,
Nellist et al. 2009) though their thermal transport properties have not yet been investigated experimentally.

Before implementing a full Monte Carlo numerical simulation, a radiation analogy was first used to analyze phonon scattering at a single sawtooth element in order to evaluate the possibility of phonon backscattering. In this analysis the nanowire interior was treated as a semi-infinite, isotropic, isothermal solid. It was assumed that random surface roughness was present on both surfaces of the sawtooth element such that they scatter phonons diffusely. Note that for Si the required random roughness to meet this condition is quite small as mentioned previously such that this assumption is both realistic and reasonable. Phonon interference effects were ignored due to the diffuse surface scattering and the short coherence length of phonons. The incident phonon irradiation on the sawtooth element was considered diffuse such that the phonon irradiation intensity $I_i$ did not depend of the angle of incidence. The rate at which phonon energy coming from the left (i.e. having a positive velocity component along the $x$-direction as drawn in Figure 2.18(a)) is incident on the sawtooth surfaces are written as

$$q_{i,+x,left} = w \frac{\delta}{\sin \theta_1} I_i \left\{ \frac{\pi}{2} \int_{\theta=0}^{\theta_1} d\phi \sin \theta \cos \theta d\theta + \int_{\theta=\theta_1}^{\pi/2} d\phi \sin \theta \cos \theta d\theta \right\}$$  \hspace{1cm} (2.61a)$$

and

$$q_{i,+x,right} = w \frac{\delta}{\sin \theta_2} I_i \left\{ \frac{\pi}{2} \int_{\theta=\theta_2}^{\phi_2} d\phi \sin \theta \cos \theta d\theta \right\}$$  \hspace{1cm} (2.61b)$$

for the left and right sawtooth faces, respectively. In Equation 2.61, $\phi_1 = 2\pi - 2\cos^{-1}\left(\tan \theta_1 / \tan \theta\right)$, $\phi_2 = 2\cos^{-1}\left(\tan \theta_2 / \tan \theta\right)$, and all angles and geometric parameters are defined as shown in Figure 2.18(a). The incident phonons produce a
diffuse scattered phonon intensity originating from the left and right sawtooth faces which can be expressed \( I_{s,\text{left}} = q_{i,+x,\text{left}} \sin \theta_\text{l} / w \delta \pi \) and \( I_{s,\text{right}} = q_{i,+x,\text{right}} \sin \theta_\text{r} / w \delta \pi \), respectively. The resulting net scattered phonon energy flux vector from each sawtooth surface is then normal to the respective surface. Projection along the x-direction of the net scattered phonon flux vector from each surface gives the x-component of the net rate of the scattered phonon energy by the sawtooth as

\[
q_{s,x} = \int \int_{\theta} \frac{2 \pi}{0} \int_{\phi} \frac{\pi}{0} I_{s,\text{right}} \sin \theta \cos^2 \theta d\theta d\phi - \int \int_{\theta} \frac{2 \pi}{0} \int_{\phi} \frac{\pi}{0} I_{s,\text{left}} \sin \theta \cos^2 \theta d\theta d\phi \].

(2.62)

The ratio of the net scattered phonon energy in the x-direction \( q_{s,x} \) to the rate of incident energy \( q_{i,+x} = q_{i,+x,\text{left}} + q_{i,+x,\text{right}} \) then serves as a measure of the directional phonon reflection from the sawtooth element as well as makes the results independent of the incident intensity. This ratio is plotted as a function of sawtooth angles \( \theta_1 \) and \( \theta_2 \) in Figure 2.18(b). The \( q_{s,x}/q_{i,+x} \) ratio was found to vary from about 0.11 to -0.67 over the entire range of angles \( \theta_1 \) and \( \theta_2 \). The sign of the ratio indicates the net x-direction of phonon scattering, where positive values corresponding to net scattering in the positive x-direction (forward scattering relative to the incident phonon energy) and negative values are associated with net scattering in the negative x-direction (backscattering of phonons relative to the incident phonon energy). For a flat surface given by \( \theta_1 = \theta_2 = 0 \), \( q_{s,x}/q_{i,+x} \) was found to be zero, which is the expected result for a completely diffuse flat surface. This zero net phonon flux along the x-direction occurs because the probability of incident phonons being forward scattered or backscattered are equal. At \( \theta_1 < \pi/20 \) and a wide \( \theta_2 \) range, \( q_{s,x}/q_{i,+x} \) was found to be small and positive, reaching a maximum value of 0.11.

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For $\theta_1 > \pi/20$, $q_{s,x}/q_{i,+x}$ was found to be negative, indicating that scattering from the sawtooth of the incident phonon flux with a positive $x$-direction velocity results in a net scattered phonon flux along the negative $x$-direction.

Figure 2.18: The single sawtooth phonon radiation analogy. (a) Schematic of the individual sawtooth phonon radiation analogy analysis. (b) The calculated $q_{s,x}/q_{i}$ ratio as a function of sawtooth angles $\theta_1$ and $\theta_2$. Reproduced with permission from A. L. Moore, S. K. Saha, R. Prasher, and L. Shi, *Applied Physics Letters* **93**, 2008, 083112, copyright 2008 American Institute of Physics.

The above analysis demonstrated that phonon backscattering from an individual sawtooth was possible. To investigate the impact of periodic sawtooth surface roughness on nanowire thermal conductivity, a Monte Carlo simulation of phonon transport within a Si nanowire with symmetric sawtooth facets and a square cross section was developed. A not-to-scale illustration of the simulation domain is shown in Figure 2.19(a), with the minimum nanowire cross section chosen to be $22 \text{ nm} \times 22 \text{ nm}$, or $d = 22 \text{ nm}$. This
diameter was chosen so as to be able to compare the obtained results for flat walls (no sawtooth roughness) with the measured thermal conductivity of a 22 nm VLS-grown Si nanowire (Li, Wu et al. 2003) as well as a previous phonon Monte Carlo study (Chen, Li et al. 2005) which attempted to simulate the same measurement data as found in Li et al.

Figure 2.19: Monte Carlo simulation domain and results. (a) 2D schematic diagram of the 3D Monte Carlo simulation domain. (b) Thermal conductance-length product and (c) thermal conductivity results of a Si nanowire with square cross section and symmetric sawtooth roughness on each of the four sidewalls. The legend in (b) also applies to (c), with the cross hair symbols in (c) representing the measured thermal conductivity of a 52 nm rough Si nanowire from Hochbaum et al. (Hochbaum, Chen et al. 2008). Reproduced with permission from A. L. Moore, S. K. Saha, R. Prasher, and L. Shi, *Applied Physics Letters* **93**, 2008, 083112, copyright 2008 American Institute of Physics.
The impact of using a square cross-section as opposed to a circular cross-section has been explored previously and found to be negligible (Chen, Li et al. 2005). The nanowire lengths were chosen to be much longer than the umklapp phonon-phonon scattering mean free path at each simulated temperature. This was done to avoid the temperature jumps noted in previous Monte Carlo phonon transport simulations (Chen, Li et al. 2005). Specifically, the nanowire lengths used in this work were 20 \( \mu \text{m} \), 15 \( \mu \text{m} \), and 10 \( \mu \text{m} \) for temperatures of 100 K, 200 K, and 300 K, respectively.

The specifics of Monte Carlo phonon simulation will not be repeated here but can be found in the literature (Mazumder and Majumdar 2001; Chen, Li et al. 2005). Briefly, the Monte Carlo approach to phonon transport modeling follows the trajectories of a representative fraction of the entire phonon population through a specified simulation domain. The tracking of only a fraction of the entire phonon population is due to the prohibitively large number of phonons within a solid compared to the processor and memory limitations of modern computing resources. Phonon polarization and dispersion are taken into account both in the phonon population calculations as well as the dependence of phonon lifetime on frequency, polarization, and temperature (Mazumder and Majumdar 2001). As the phonons travel within the simulation domain they are subjected to umklapp and normal phonon-phonon scattering, phonon-boundary scattering, and phonon-impurity scattering (Mazumder and Majumdar 2001). Scattering by internal processes (phonon-phonon and impurity scattering) is dictated by a comparison between the simulation time step, the phonon lifetime calculated for a given phonon from perturbation theory, and a random number produced from the simulation’s
random number generator (Mazumder and Majumdar 2001). Boundary scattering, by comparison, occurs when the phonon trajectories interact with the specified simulation domain walls and does not rely on a calculated lifetime. In the two previously reported Monte Carlo simulations of phonon transport in Si thin films and nanowires (Mazumder and Majumdar 2001; Chen, Li et al. 2005), the surfaces were treated as flat and the effects of surface roughness were incorporated by a user-defined specularity \( p \) between 0 and 1. A randomly drawn number would then be compared to the prescribed \( p \) to determine if the incident phonon would be emitted from the struck surface specularly or diffusely with regard to its angle of incidence (Mazumder and Majumdar 2001; Chen, Li et al. 2005). For diffuse surface scattering, the direction of reflection was randomized by redistributing the velocity components at the surface via random numbers while maintaining the phonon group velocity (Mazumder and Majumdar 2001; Chen, Li et al. 2005). Thus, phonon scattering from surfaces was treated statistically in these earlier works rather than incorporating the specific nature of the surface.

For the Monte Carlo simulations in this work, periodic sawtooth elements were added to the four flat side wall surfaces of the square cross-section as shown in Figure 2.19(a). The sawtooth height (\( \delta_1 \)) and length (\( \delta_2 \)) were varied from 2 nm to 4 nm to examine the impact of both sawtooth size and scattering angle. Considering the small dominant phonon wavelength for Si as described above, each sawtooth face was set to scatter phonons diffusely according to the diffuse surface methods commonly used in Monte Carlo simulation of thermal radiation transport (Siegel and Howell 2002). Except for the modified surface morphology and the use of a simplified, more efficient algorithm for phonon-phonon and impurity scattering, we have followed Chen et al.’s Monte Carlo
methods for Si nanowires (Chen, Li et al. 2005). Each simulated case was run three
times with different seed values for the random number generator for each run. The data
presented here is the average of three runs, with errors bars representing the
corresponding random uncertainty at 90% confidence.

The thermal conductivity values obtained for the case of flat, specular walls ($\delta_1 = 0$) were 1061, 445, and 133 W/m-K at 100 K, 200 K, and 300 K, respectively. These
values are in good agreement with literature values for bulk Si (Glassbrenner and Slack
1964) and the bulk Monte Carlo simulation results of Chen et al. (Chen, Li et al. 2005).
For $\delta_1 = 0$ and diffuse walls, the resulting thermal conductivity values were found to be
6.64, 11.85, and 12.13 W/m-K, respectively, at 100 K, 200 K, and 300 K and represent
the $\kappa_{\text{diffuse}}$ limit discussed previously.

The cross-section area $A$ of the sawtooth nanowires is variable and not well
defined. Thus, in order to make an accurate comparison of the simulated cases the
thermal conductance ($G$)-length ($L$) product for the symmetric sawtooth surfaces of
different $\delta_1$ and $\delta_2$ values were plotted as shown in Figure 2.19(b). For the two cases with
longer sawtooth length $\delta_2$, the $G$-$L$ product is higher than for the flat and diffuse case of
$\delta_1 = 0$ nm. This is due to the increase in the effective cross-sectional area ($A$) brought
about by the addition of the sawtooth features to the nominally square cross-section.
However, when $\delta_2$ is decreased from 4 nm to 2 nm, the $G$-$L$ product becomes lower than
$G_{\text{diffuse}}$ despite the increase in cross-sectional area brought on by the sawtooth elements.
Further, the smallest $G$-$L$ product was found for the $\delta_1 = 4$ nm, $\delta_2 = 2$ nm case with the
highest sawtooth angle $\theta$. This is in general agreement with the backscattering of
phonons by the added sawtooth surface roughness as suggested by the more negative $q_{s,x}/q_{i,+x}$ ratio for larger $\theta_1$ and $\theta_2$ values of a single sawtooth in Figure 2.18(b). However, the backscattering effect for periodic sawtooth roughness can be much more complicated than suggested by the analysis of an individual sawtooth element. For periodic roughness, multiple phonon-surface scattering events can occur between opposing sawtooth surfaces which can limit the phonon mean free path and make the assumption of diffuse incident phonon energy used in the radiation analogy invalid.

Despite some ambiguity as to a proper treatment of the variable cross-sectional area, if $A$ is defined as the ratio between the volume and the length of the nanowire a thermal conductivity $\kappa$ can be calculated from the thermal conductance. The obtained $\kappa$ values of the flat and sawtooth nanowires are shown in Figure 2.19(c). It was found that the thermal conductivities of the sawtooth nanowires were all below $\kappa_{\text{diffuse}}$ of the 22 nm x 22 nm flat-walled nanowire. It should be noted that $\kappa_{\text{diffuse}}$ for the 22 nm flat-walled nanowire is expected to be lower than $\kappa_{\text{diffuse}}$ for flat-walled nanowires with the same effective $A$ as the sawtooth nanowires. Additionally, the lowest thermal conductivity values were obtained from the taller sawtooth height ($\delta_1 = 4$ nm), with the higher angle case ($\delta_1 = 4$ nm, $\delta_2 = 2$ nm) demonstrating the lowest thermal conductivity of all cases. Similar sawtooth angle dependence was observed for the shorter sawtooth height of $\delta_1 = 2$ nm, with the lowest sawtooth angle case ($\delta_1 = 2$ nm, $\delta_2 = 4$ nm) giving the highest thermal conductivity of the sawtooth cases simulated. In comparison to Si nanowire measurement results, for the two cases with a larger $\delta_1$ of 4 nm the obtained thermal conductivities are rather close to the measurement result of the 22 nm VLS nanowire (Li,
Wu et al. 2003), but still considerably higher than those for rough etched Si nanowires of 50 - 75 nm diameter measured by Hochbaum et al. (Hochbaum, Chen et al. 2008). This suggests that for the etched Si nanowires, classical phonon scattering from rough surfaces alone is insufficient to explain their measurement result of extreme thermal conductivity suppression.

These results show that surface engineering can be utilized to reduce thermal conductivity below $\kappa_{\text{diffuse}}$ in silicon nanowires. It should be noted that if the details of the sawtooth surface roughness are ignored and the surface is represented with a specularity parameter $p$, a negative $p$ in the range between 0 and -1 would be required in Equation 2.59 to reduce the phonon mean free path below the nanowire diameter and give $\kappa < \kappa_{\text{diffuse}}$. Thus, discretion should be used when attempting to describe a nanostructure surface in terms of the single parameter $p$ from Ziman’s formula (Equation 2.59) as the carrier-surface interactions may be fundamentally different from those for scattering from random surface roughness as modeled in Ziman’s treatment.

CONCLUSION

Throughout this chapter, the focus has been on using solutions of the BTE in various forms to describe energy transport in nanostructures. In some cases such as the modeling of electrical transport in nanowires, the transport coefficient expressions found from RTA-based BTE solutions worked well in obtaining valuable information regarding carrier behavior. For the modeling of SiO$_2$-supported graphene thermal conductivity, however, the RTA-based phonon BTE model failed to capture the relevant physics and
could not match the experimental results. Instead, the full quantum mechanical solution was necessary, illustrating the limitations of the RTA in some circumstances for the modeling of nanoscale energy transport. Finally, indirect, statistical solution of the BTE using Monte Carlo simulation was demonstrated for the case of Si nanowires with and without sawtooth surface roughness elements, illustrating yet another approach to exploring nanoscale energy transport through the BTE. Together, these works serve to demonstrate the development, use, and limitations of RTA-based nanoscale energy transport models as a tool towards developing functional nanostructures for thermal and thermoelectric applications.
Chapter 3: Evaluation of Measurement Methods in Nanoscale Heat Transfer

In Chapter 2, analytical and numerical models were used to analyze and explain the measured thermal and thermoelectric properties of nanowires and oxide-supported graphene. These analyses were conducted with the implicit assumption that the measurement data in question were accurate. In this chapter, analytical and numerical methods are used to study several measurement methods and designs used in the experimental investigation of nanoscale energy transport.

RAMAN MEASUREMENT OF SUSPENDED AND SUPPORTED CVD GRAPHENE

The first experiment to be considered is measurement of the thermal conductivity of suspended and Au-supported single layer graphene grown by chemical vapor deposition (CVD) using Raman spectroscopy. Graphene obtained by mechanical exfoliation as in the measurement by Seol et al. (Seol, Jo et al. 2010) is difficult to utilize for mass production of functional devices. In response, the synthesis of large-area, high-quality graphene from CVD on a thin film transition metal catalyst such as nickel (Ni) or copper (Cu) has become an area of intense research (Kim, Zhao et al. 2009; Li, Cai et al. 2009; Reina, Jia et al. 2009). Despite its device potential, the thermal conductivity of CVD graphene in both the suspended and substrate-supported states has remained unknown. This is in part due to the experimental difficulties associated with the ultrathin nature of graphene in general, although two recent studies on thermal conduction in
exfoliated graphene have been presented (Balandin, Ghosh et al. 2008; Seol, Jo et al. 2010). The later of these by Seol et al. is the study of oxide-supported graphene discussed in Chapter 2. The other experimental work (Balandin, Ghosh et al. 2008) utilized a micro-Raman spectroscopy optical measurement technique and obtained a thermal conductivity value of about 5000 W/m-K for mechanically exfoliated suspended monolayer graphene, about two times higher than the basal plane thermal conductivity typically found for high quality graphite (Slack 1962). However, the optical absorption of ~12 % used in their work (Balandin, Ghosh et al. 2008) was based on an optical absorption model in conjunction with graphite-based calibration and is considerably higher than the 2.3 % optical absorption from optical transmission measurement of monolayer graphene (Nair, Blake et al. 2008). This discrepancy highlights the necessity of measuring the optical absorption of graphene directly in these types of optical heating experiments. In addition, the thermal conductivity of the SiO$_2$-supported graphene regions was assumed to be the same as that of the suspended segment (Balandin, Ghosh et al. 2008). Later, the experiments by Seol et al. (Seol, Jo et al. 2010) demonstrated that the thermal conductivity of SiO$_2$-supported graphene could be considerably lower than values for suspended graphene. Hence, besides the scientific and application-related motivations for studying the thermal conductivity of CVD-derived graphene, there remained room for improvement on the experimental methods used in optics-based graphene thermal conduction studies.

In experiments led by Dr. Weiwei Cai (Cai, Moore et al. 2010), a modified approach using micro-Raman spectroscopy was developed for the measurement of thermal conductivity for large-area, monolayer graphene grown by CVD on Cu utilizing
the growth method of Li et al. (Li, Cai et al. 2009). In combination with the experimental analysis led by the author (Arden Moore), the thermal conductivities of both the suspended and Au-supported CVD graphene regions were obtained from the resulting measurement data. Briefly, following growth the CVD graphene was transferred to a ~500-nm thick Au film on a 300-nm thick low-stress silicon nitride (SiN$_x$) membrane supported at the edges by a Si frame. The Au/SiN$_x$ membrane consisted of an array of 3.8 µm diameter holes at a pitch of 10 µm over which regions of the transferred graphene could be suspended. In this configuration, the optical transmission through the suspended graphene was able to be measured directly using a semiconductor laser power meter placed under the Au/SiN$_x$ support. Additionally, the circular hole geometry for the suspended graphene region matched the radial symmetry of the heat flux resulting from the heating laser spot at the center of the suspended graphene. The quality and number of layers of the graphene films were determined by micro-Raman spectroscopy (Li, Cai et al. 2009) which indicated high quality monolayer graphene samples. Further details on the graphene growth and experimental setup can be found elsewhere (Cai, Moore et al. 2010).

An illustration of the suspended graphene measurement is shown in Figure 3.1(a). During the thermal measurement, a 532 nm laser beam is focused through an objective lens on either the center of the suspended graphene or the area of the graphene supported on the Au/SiN$_x$ membrane. The power absorbed by the suspended graphene $Q$ was obtained as the difference between the power transmitted through an empty hole $P_{empty}$ and that transmitted through the graphene sample as measured by the power meter.
described above, giving an optical absorption of $3.3 \pm 1.1\%$ at 532 nm wavelength. For measurements of the thermal conductivity the Au-supported graphene regions, the laser beam was simply moved away from the hole and onto a graphene region supported on the Au/SiN$_x$ membrane. The laser power absorbed by the supported graphene was taken to be twice that of the suspended graphene at the same laser power due to reflection from the Au surface. The calibrated linear dependence (Calizo, Balandin et al. 2007) of the red-shift of the Raman G peak as measured by the laser beam was used to obtain the rise in graphene temperature for each laser power measured. During these measurements the stage was kept at ambient temperature. The laser beam’s power profile was found to be well described by a Gaussian function $\exp(-r^2/r_0^2)$, where $r$ is the radial distance from the beam spot center and $r_0$ is the radius of the beam spot. Beam spot radius $r_0$ values of 0.17 µm and 0.28 µm were determined experimentally for the 100× and 50× objectives used in this work, respectively. The measured temperature rise versus absorbed laser power for the suspended and Au-supported CVD graphene measurements are shown in Figure 3.1(b), with the G-peak versus temperature calibration curve as an inset. Details on the G peak calibration procedure as well as the experimental determination of the laser beam shape and spot sizes can be found elsewhere (Cai, Moore et al. 2010).
Figure 3.1: Raman measurement of graphene thermal transport. (a) Illustration of the experimental setup for the suspended graphene thermal conductivity measurement. For measurement of the supported graphene, the beam spot is moved to a graphene region on the Au/SiN$_x$ membrane. (b) Measured Raman G peak shift (left axis) and associated graphene temperature (right) for the suspended and Au-supported CVD graphene obtained from the 100x and 50x objectives as a function of the absorbed laser power.Inset: Calibration of the measured red-shift of the Raman G peak at low laser power with adjusted stage temperature for both supported and suspended graphene. Reproduced with permission from W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, and R. Ruoff, *Nano Letters*, DOI: 10.1021/nl9041966, 2010, copyright 2010 American Chemical Society.

The analysis if the Au-supported graphene measurement will be presented first, followed by the analysis of the suspended graphene measurement. To begin, it was determined that that direct laser heating of the Au film beneath the graphene produced a
negligible temperature rise in the Au film itself. This was calculated as follows: for simplicity, consider a flat top laser beam with radius $r_0$ incident on the Au surface. The conduction thermal resistance of the Au film $R_{Au}$ is given by $R_{Au} \approx 1/(4\kappa_{Au} r_0^2)$, where $\kappa_{Au}$ is the Au thermal conductivity. The temperature rise $\Delta T_{Au}$ of the Au layer is then $\Delta T_{Au} = Q_{Au} R_{Au}$, where the heat absorbed by the Au is $Q_{Au}$. For the maximum incident laser power used in the experiment with the 100× objective lens, 3 % absorptivity (Incropera and Dewitt 2002) for the Au layer, and $\kappa_{Au}$ conservatively assumed to be reduced from the bulk value of 317 W/m-K (Incropera and Dewitt 2002) to 100 W/m-K, the maximum temperature rise in the Au was found to be approximately 4 K. This is much smaller than the 114 K temperature rise measured at the same incident laser power with the spot focused on the Au-supported graphene. Hence, the temperature rise measured by the laser beam is overwhelmingly from the supported graphene, while the underlying Au film can be safely treated as an isothermal environment at the ambient stage temperature.

Next, heat losses from the graphene to the environment during measurement are considered. As a worst case scenario, the maximum radiation heat transfer coefficient is obtained from $g_{rad} = \sigma_{SB} T^3$, where $\sigma_{SB}$ is the Stefan-Boltzmann constant. At the upper limit of the measured temperature range at 650 K, the obtained $g_{rad}$ reaches a maximum value of 15 W/m²-K. Again assuming a worst case scenario where the energy accommodation coefficient of the surrounding air molecules is 1 and ignoring the air diffusive thermal resistance, the maximum air interface thermal conductance per unit area
is given by $g_{\text{air}} = (n_{\text{air}} v_{\text{air}} / 4)C$ where $n_{\text{air}} = P/k_B T_{\text{air}}$ is the number density of air molecules, $v_{\text{air}} = (3k_B T_{\text{air}} / m)^{1/2}$ is the air molecule root mean square velocity, $C = 5k_B / 2$ is the specific heat of diatomic molecules such as O\textsubscript{2} and N\textsubscript{2}, $m$ is air molecule mass, and $P$ and $T_{\text{air}}$ are the pressure and temperature of air molecules, respectively. The air interface conductance $g_{\text{air}}$ increases with decreasing $T_{\text{air}}$, approaching a maximum value of $1.08 \times 10^5$ W/m\textsuperscript{2}-K for the lower limit of 300 K. This is several orders of magnitude larger than found for radiation losses such that $g_{\text{rad}}$ is negligible by comparison. The obtained maximum $g_{\text{air}}$ value was then used to calculate the heat loss to the air $q_{\text{air}} = \int_0^R 2\pi r g_{\text{air}} (T(r) - T_a) dr$. Here, $T(r)$ is the graphene temperature profile, the calculation of which will be presented shortly. Towards the lower end of the measured temperature range with $T_m = 400$ K, the maximum possible $q_{\text{air}}$ was found to be 0.026 and 0.033 mW for the 100× and 50× objectives, respectively. These are five and six times smaller than the measured absorbed laser power $Q$ at $T_m = 400$ K for the 100× and 50× objectives in the suspended graphene measurement, respectively. In addition, using $g = g_{\text{air}} = 1.08 \times 10^5$ W m\textsuperscript{-2} K\textsuperscript{-1} in Equation 3.8 gives thermal conductivity values that are within 6% of the values in Figure 3.2. As will be shown in the following section, the interface thermal conductance found for the Au-supported graphene measurement is orders of magnitude larger than that calculated for the maximum possible heat loss to air. Ideally this experiment would be carried out in vacuum, but there are significant experimental complexities that would need to be solved in order for this to be possible.

As shown in Seol et al. (Seol, Jo et al. 2010), the mean free paths of phonons in supported graphene can be limited by substrate interactions to be smaller than the laser
beam spot sizes used in this work. Under these conditions the phonon transport in the 
Au-supported graphene is diffusive, making it possible to obtain the temperature 
distribution from the following cylindrical heat diffusion equation

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{dT}{dr} \right) - \frac{g}{\kappa_s t_G} (T - T_a) + \frac{\dot{q}''(r)}{\kappa_s} = 0
\]  \tag{3.1}

where \(T_a\) is the ambient temperature as discussed above in regards to the Au supporting 
film, \(r\) is the radial position measured from the center of the laser beam, \(t_G = 0.335\) nm is 
the accepted monolayer graphene thickness value used in literature, \(\kappa_s\) is the thermal 
conductivity of the supported graphene, and \(g\) is the total interface thermal conductance 
per unit area between the supported graphene and its environment (the Au supporting 
film on one side, air molecules on the other). In Equation 3.1, \(\dot{q}''(r)\) is the volumetric heating 
associated with the absorbed laser power and is expressed as

\[
\dot{q}''(r) = \frac{q_0''}{t_G} \exp \left( -\frac{r^2}{r_0^2} \right)
\]  \tag{3.2}

where the exponential form is due to the Gaussian-like beam shape and \(q_0''\) is the peak 
absorbed laser power per unit area at the center of the beam spot. The total absorbed 
laser power \(Q\) from the laser beam is then

\[
Q = \int_0^\infty q_0'' \exp \left( -\frac{r^2}{r_0^2} \right) 2\pi rdr.
\]  \tag{3.3}

Changing the temperature variable to \(\theta \equiv (T-T_a)\) and grouping terms into a dimensionless 
variable \(z = \sqrt{\frac{g}{\kappa_s t_G} r}\), Equation 3.1 becomes a non-homogeneous modified Bessel’s 
equation
\[ z^2 \frac{\partial^2 \theta}{\partial z^2} + z \frac{\partial \theta}{\partial z} - z^2 \theta = -\frac{q_0'' z^2}{g} \exp \left( -\frac{z^2}{z_0^2} \right). \] (3.4)

The solution to Equation 3.4 is given as the linear combination of the homogeneous and particular solutions (Greenberg 1998)

\[ \theta(z) = C_1 I_0(z) + C_2 K_0(z) + \theta_p(z) \] (3.5)

where the two homogeneous solutions \( I_0(z) \) and \( K_0(z) \) are the zero-order modified Bessel functions of the first and second kind, respectively. The particular solution \( \theta_p(z) \) is given by the variation of parameters method (Greenberg 1998)

\[ \theta_p(z) = I_0(z) \int \frac{K_0(z) \frac{q_0''}{g} \exp \left( -\frac{z^2}{z_0^2} \right)}{-I_0(z) K_1(z) - K_0(z) I_1(z)} \, dz - K_0(z) \int \frac{I_0(z) \frac{q_0''}{g} \exp \left( -\frac{z^2}{z_0^2} \right)}{-I_0(z) K_1(z) - K_0(z) I_1(z)} \, dz \] (3.6)

where \( I_1(z) \) and \( K_1(z) \) are the first-order modified Bessel functions of the first and second kind, respectively. Boundary conditions are \( \frac{d\theta}{dz} \bigg|_{z=0} = 0 \) and \( \theta(z \rightarrow \infty) = 0 \). These require that \( C_2 = 0 \) and \( C_1 = -\lim_{z \rightarrow \infty} \frac{\theta_p(z)}{I_0(z)} \), where the expression for \( C_1 \) does indeed approach a constant value for large \( z \).

The measured temperature rise \( \theta_m \) in the graphene as determined by the Gaussian-like laser beam is

\[ \theta_m = \frac{\int_0^\infty \theta(r) \exp \left( -\frac{r^2}{r_0^2} \right) r \, dr}{\int_0^\infty \exp \left( -\frac{r^2}{r_0^2} \right) r \, dr}. \] (3.7)
If the measured thermal resistance is defined as \( R_m = \theta_m / Q \), then from Equation 3.3 and Equation 3.7 \( R_m \) is expressed as

\[
R_m = \frac{\int_0^\infty \left( -I_0(z) \lim_{z \to \infty} \frac{\theta_p(z)}{I_0(z)} + \theta_p(z) \right) \exp \left( -\frac{r^2}{r_0^2} \right) rdr}{\int_0^\infty \exp \left( -\frac{r^2}{r_0^2} \right) rdr \int_0^\infty q_0(z) \exp \left( -\frac{r^2}{r_0^2} \right) 2\pi rdr}.
\]  

(3.8)

The slopes of \( \theta_m \) and \( Q \) measured for Au-supported graphene gave \( R_m \) values of \((2.37 \pm 0.81) \times 10^5\) and \((1.05 \pm 0.37) \times 10^5\) K/W, respectively, for the 100x and 50x objective lenses. The measured \( R_m \) for each of the objectives and their ratio can be used to determine the Au-supported graphene thermal conductivity \( \kappa_s \) and the interface conductance \( g \). The random uncertainty in five measurements of the \( \theta_m-Q \) slopes as well as calibration (or bias) errors associated with measuring \( \theta_m \) and \( Q \) are considered in the uncertainties of the \( R_m \) values, whereas only the random uncertainties need to be propagated into the uncertainty of the \( R_m \) ratio (Coleman and Steele). The ratio of \( R_m \) for the 100x objective to \( R_m \) for the 50x objective was determined to be \( 2.26 \pm 0.23 \). Based on Equation 3.8, the \( R_m \) ratio only depends on \( z \) which in turn depends on the \( g/\kappa_s \) ratio. Thus, the \( R_m \) ratio determined from the measurement data can be used to determine \( g/\kappa_s \) uniquely. Knowing this ratio, the interface thermal conductance is then determined uniquely by adjusting \( g \) in Equation 3.8 to match the \( R_m \) value measured with one of the objective lenses. Knowing \( g \) as well as the \( g/\kappa_s \) ratio, the thermal conductivity of the Au-supported graphene \( \kappa_s \) is easily found. Following this procedure yielded \( \kappa_s \) of \((370 +650/-320)\) W/m-K and \( g \) of \((28 +16/-9.2)\) MW/m²-K. The thermal conductivity of the
Au-supported CVD graphene is comparable to the room-temperature thermal conductivity range of 479 - 680 W/m-K measured for SiO$_2$-supported exfoliated graphene by Seol et al. (Seol, Jo et al. 2010). The obtained thermal interface conductance is also comparable to the thermal interface conductance values of ~ 50 and 83 MW/m$^2$ K reported in literature between graphite and evaporated Al (Schmidt, Chen et al. 2008) and for SiO$_2$-embedded graphene (Chen, Jang et al. 2009), respectively. The obtained thermal interface conductance is also much larger than the interface thermal conductance between the graphene and surrounding air molecules as found previously.

Analysis of the Raman measurement for the suspended graphene is now presented. In this measurement, the laser beam was focused on the center of the circular suspended region and the measured thermal resistance is

$$R_m = R_g + R_c$$  \hspace{1cm} (3.9)

where $R_g \equiv (T_m - T_1)/Q$ is defined as the equivalent thermal resistance of the suspended graphene outside of the laser spot heat generation region, $R_c \equiv (T_i - T_u)/Q$ is the contact thermal resistance between the surrounding Au/SiN$_x$ support and the contacted graphene, and $T_i$ is the temperature at the edge of the suspended graphene region. Because the hole radius $R$ (1.9 $\mu$m) is much larger than the beam spot sizes $r_0$ of 0.17 $\mu$m and 0.28 $\mu$m, the optical heating term $q$" in Equation 3.1 was neglected in the following analysis of the supported graphene region during laser measurement of the suspended region. With $q" = 0$, the supported graphene with $r > R$ can be treated as a circular fin whose temperature distribution is given by the homogeneous solution components of Equation 3.5 (Mills).
Using the boundary conditions $\theta(z \to \infty) = 0$ and $Q(1 - \exp(-R^2 / r_0^2)) = -2\pi R t G \kappa_s \frac{\partial T}{\partial r} \bigg|_R$, the temperature distribution in the supported area of the graphene was expressed as

$$\theta(z) = \frac{Q(1 - \exp(-R^2 / r_0^2)) K_0(z)}{2\pi R \sqrt{gt \kappa_s}} \frac{K_0(z_R)}{K_1(z_R)}, \text{ for } r \geq R \quad (3.10)$$

where $z_R$ is the value of $z$ at $r=R$. The thermal contact resistance was then determined from

$$R_c = \frac{\theta(z_R)}{Q} = \frac{(1 - \exp(-R^2 / r_0^2)) K_0(z_R)}{2\pi R \sqrt{gt \kappa_s}} \frac{K_0(z_R)}{K_1(z_R)}. \quad (3.11)$$

Substituting the obtained $\kappa_s$ and $g$ values found in the Au-supported graphene measurement and analysis described above into Equation 3.11 gave $R_c \approx (4.4 +8.4/-2.0) \times 10^4 \text{ K/W}$.

If phonon transport in the suspended graphene monolayer is diffusive and heat loss from the graphene to the environment is small then the solution of Equation 3.1 for $g = 0$ gives the temperature distribution of the suspended graphene during measurement.

With the boundary conditions of $T(r=R) = T_1$ and $Q(1 - \exp(-R^2 / r_0^2)) = -2\pi R \kappa_G \frac{dT}{dr} \bigg|_R$, the temperature distribution in the suspended graphene was found to be

$$T(r) = T_1 + \frac{Q}{2\pi \kappa_G} \ln \left( \frac{R}{r} \right) \beta(r), \text{ for } r \leq R \quad (3.12)$$

where
\[
\beta(r) = \left[ 1 + \frac{Ei(-r^2/r_0^2) - Ei(-R^2/r_0^2)}{2\ln\left(\frac{R}{r}\right)} \right]^{(3.13)}
\]

and \(Ei(x)\) is the exponential integral.

Similar to Equation 3.7, the graphene temperature measured by the Gaussian-like Raman laser is

\[
T_m = \frac{\int_0^R T(r)\exp\left(-\frac{r^2}{r_0^2}\right) rdr}{\int_0^R \exp\left(-\frac{r^2}{r_0^2}\right) rdr}. \quad (3.14)
\]

From the diffusive solution for the temperature profile the equivalent thermal resistance of the suspended graphene as defined previously was expressed as a function of the beam spot size \(r_0\) and the suspended graphene thermal conductivity \(\kappa\), specifically

\[
R_g \equiv \frac{T_m - T_1}{Q} = \alpha \frac{\ln(R/r_0)}{2\pi\kappa g} \quad (3.15)
\]

where

\[
\alpha = \frac{T_m - T_1}{T_0 - T_1} \beta(r_0). \quad (3.16)
\]

In Equation 3.16, \(T_0\) is the temperature at the edge of the beam spot \((r = r_0)\). The temperature ratio \((T_m - T_1)/(T_0 - T_1)\) as calculated using Equations 3.12 - 3.14 is a function of \(r_0\) only and increases from 1.02 to 1.03 when \(r_0\) increases from 0.17 \(\mu m\) for the 100\(\times\) objective to 0.28 \(\mu m\) for the 50\(\times\) objective. For the hole radius of \(R = 1.9 \mu m\) used in this
work and the measured $r_0$ values, the $\alpha$ factor was found to be 0.98 and 0.97 for the 100× and 50× objective lenses, respectively.

Because of the nonlinear $T_m$ versus $Q$ behavior measured for the suspended graphene at high $T_m$ as shown in Figure 3.1(b), the measured thermal resistance $R_m$ was determined from $R_m = (T_m - T_a)/Q$ for each data point instead using the total $T_m$-$Q$ slope as done for the linear data obtained from the Au-supported graphene measurement. The obtained $R_m$ values for the suspended graphene were found to be one order of magnitude larger than the thermal contact resistance determined above.

Based on Equation 3.9 and Equation 3.15, $R_m$ for the suspended graphene should decrease linearly with $\alpha \ln(R/r_0)$ and be equal to the thermal contact resistance at $\alpha \ln(R/r_0) = 0$. However, when this approach was tried using the measurement data at similar $T_m$ from the two objectives with different $r_0$ values, linear extrapolation to $\alpha \ln(R/r_0) = 0$ resulted in a negative thermal contact resistance, the magnitude of which decreased with increasing $T_m$. This behavior was attributed to non-diffusive, quasi-ballistic transport occurring for low frequency phonons with mean free paths longer than the beam spot sizes (Klemens 2001). Physically, the photoexcited electron-hole pairs generated by the incident laser lose their energy to high frequency optical phonons on a time scale of ~100 fs (Ma, Stenger et al. 2004) which corresponds to a length scale of ~100 nm that is comparable to or smaller than the two $r_0$ values in this work. Low frequency phonons like those mentioned above are then not thermalized with the high energy carriers within $r_0$ and thus carry less heat than what is inherently assumed in the
diffusive transport analysis. Consequently, the suspended graphene thermal resistance $R_g$ has an additional ballistic resistance component ($R_b$) in addition to the diffusive component ($R_d$) determined from Equation 3.15 such that $R_g \approx R_d + R_b$ (Chen 1997; Chen 1998; Prasher 2005; Saha and Shi 2007; Siemens, Li et al. 2010). The ballistic thermal resistance is proportional to the phonon mean free path and inversely proportional to $r_0$ such that the measured thermal resistance contains a larger ballistic resistance contribution for the smaller $r_0$ at similar $T_m$. This difference in the ballistic thermal resistance between the two spot sizes used in the experiment then resulted in a negative intercept at $\alpha \ln(R/r_0) = 0$. As $T_m$ increases the magnitude of the negative intercept decreases because the increased phonon-phonon scattering that occurs at higher temperatures reduces the phonon mean free path of the low frequency phonons, thus causing the ballistic thermal resistance to have a smaller role in determining the measured graphene thermal resistance.

Ignoring the ballistic resistance component, the lower bound of the thermal conductivity of the suspended graphene was calculated from

$$\kappa = \frac{\ln(R/r_0)}{2\pi G (R_m - R)} \alpha.$$

(3.17)

The obtained $\kappa$ results from this method were similar for measurement of CVD graphene suspended over four different 3.8 µm diameter holes. Figure 3.2 plots the $\kappa$ of the graphene monolayer suspended over one of the four holes versus the measured $T_m$ at each laser heating rate. The decreasing $\kappa$ with increasing $T_m$ trend suggests increased anharmonic phonon-phonon scattering of the phonons that contribute to the measured $\kappa$.  

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As discussed above, the larger \( r_0 \) associated with the 50x objective results in a smaller contribution from the ballistic resistance component than for the 100x objective. Thus, the \( \kappa \) values obtained with the 50x objective are higher than those obtained with the 100x objective for \( T_m < 450 \) K. As temperature increases the phonon mean free paths become smaller, resulting in a reduced ballistic component such that the \( \kappa \) values obtained with the two different objectives for \( T_m > 450 \) K approach similar values. As temperature continues to increase these values should approach the intrinsic thermal conductivity of the suspended graphene.

In addition, it should be noted that phonons with mean free path longer than the hole radius \( R \) are not heated due to their lack of scattering/interaction with higher energy carriers, i.e. photoexcited electron-hole pairs or other higher energy phonons. As a result, these phonons remain at the ambient temperature and do not contribute to thermal transport in the finite-sized suspended graphene. Due to this effect, the intrinsic thermal conductivity of suspended graphene is expected to increase with sample size based on the theoretical model of Klemens (Klemens 2001). Even with this finite sample size limitation, the obtained thermal conductivity values shown in Figure 3.2 are higher than thermal conductivity values for the basal plane of pyrolytic graphite reported in literature (Slack 1962; Hooker, Ubbelohde et al. 1965; Taylor 1966).
Figure 3.2: Thermal conductivity of suspended CVD graphene plotted versus the measured graphene temperature. Also shown are basal plane thermal conductivity data for pyrolytic graphite from literature (Slack 1962; Hooker, Ubbelohde et al. 1965; Taylor 1966). Reproduced with permission from W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, and R. Ruoff, Nano Letters, DOI: 10.1021/nl9041966, 2010, copyright 2010 American Chemical Society.

The Raman thermal measurement presented and analyzed here addressed two critical issues present in earlier work on suspended graphene; namely, direct measurement of the graphene optical absorption and consideration of the thermal contact resistance at the boundary of the suspended graphene. The thermal conductivity of the Au-supported CVD graphene and its interface thermal conductance were also obtained through a combination of experimental and analytical methods. In this way, Raman
measurement presents a viable non-contact means of exploring thermal transport in atomically thin films. However, there remain some limitations and room for further improvement. Reduction of heat loss to air could increase the accuracy of the measurement and the validity of the associated conduction analysis. Additionally, reducing the rather large relative uncertainty in the measured temperature and absorbed laser power would give reduced uncertainty in the obtained properties as well. These limitations currently make measurements near room temperature or at low laser powers impractical. Finally, measurement of larger suspended graphene regions might allow for the slope-intercept method to be employed in determining the thermal contact resistance without complication from non-trivial ballistic thermal resistance contributions.

**FINITE ELEMENT ANALYSIS OF SUSPENDED MICRODEVICES**

The use of microfabricated devices to measure the thermal and thermoelectric transport properties of nanostructures was mentioned several times in the previous chapter. These types of devices typically use patterned metal lines as resistance thermometers and as a means of creating temperature gradients with Joule heating. For nanowires in particular the device and sample are usually suspended above the main substrate in order to allow for an accessible energy conservation analysis to be made. Measurements are performed in a vacuum-pumped cryostat with radiation shielding to reduce heat losses from convection and radiation. The sample thermal conductance is then determined from the measured temperature gradient, known heat generation, and the associated heat conduction analysis of the suspended device. Though this basic measurement approach has appeared several places in literature (Li, Wu et al. 2003; Shi, Li et al. 2003; Zhou, Jin et al. 2005; Yu, Saha et al. 2006; Mavrokefalos, Pettes et al.
2007; Zhou, Szczech et al. 2007; Boukai, Bunimovich et al. 2008; Chen, Hochbaum et al. 2008; Hochbaum, Chen et al. 2008; Mavrokefalos, Moore et al. 2009; Moore, Pettes et al. 2009; Sultan, Avery et al. 2009; Seol, Jo et al. 2010; Zhou, Moore et al. 2010) and from various research groups, the specific device designs and their associated conduction analyses can differ significantly. Thus, for different designs the accuracy depends not just on the experimental uncertainties but also on the validity of the associated conduction analysis. With this in mind, several suspended microdevice designs were reconstructed as finite element models in order to evaluate their thermal behavior and the accuracy of their respective conduction models from which sample thermal conductance is ultimately determined. To accomplish this, the measurement of samples with known, specified thermal conductance were simulated and the resulting temperature information from the resistance thermometer regions used in the respective device analysis. The thermal conductance values for the sample and supporting beams obtained from this process were then compared to the known thermal conductance values and sources of discrepancy investigated. The results of these studies for several device designs used by in this work as well as found in literature are presented in the following sections.

**Serpentine Heater Device**

The first suspended microdevice design to be presented is one developed by the Shi group at UT-Austin which uses two SiN$_x$-based membranes suspended over a through-substrate hole by six SiO$_2$-Pt-SiN$_x$ beams. Two platinum (Pt) electrodes and a serpentine Pt resistance thermometer are patterned on each membrane, with the beams and serpentine heater regions covered by SiO$_2$ to protect against unwanted shorting during sample preparation. The through-substrate hole beneath the suspended membranes allows for TEM characterization to be performed on the sample following
measurements. SEM images of the device design under investigation are shown in Figure 3.3.

![Figure 3.3: Suspended microdevice with a serpentine heater developed by the Shi group for thermal and thermoelectric characterization of nanostructures. (a) Full view of the suspended region. Details of the suspended membrane area are shown in (b), where the four bright rectangles at the sample-electrode intersections are amorphous carbon-Pt contacts from beam-induced deposition used to improve the electrical and/or thermal contact resistances.](image)

Devices with this design were used to measure the CrSi$_2$, Bi$_2$Te$_3$, and large diameter InSb nanowires discussed in Chapter 2 as well as the bismuth (Bi) nanowires in Chapter 4 and the most of the higher manganese silicide (HMS) nanostructures in Chapter 5. Similar designs which use patterned electrodes and serpentine lines on suspended SiN$_x$ membranes have been used extensively in the characterization of nanostructures (Li, Wu et al. 2003; Shi, Li et al. 2003; Zhou, Jin et al. 2005; Yu, Saha et al. 2006; Chen, Hochbaum et al. 2008; Hochbaum, Chen et al. 2008) though often
without the protective oxide layer or four-probe electrical conductivity capabilities. The conduction and measurement analyses associated with this type of design are available elsewhere (Shi, Li et al. 2003; Yu, Saha et al. 2006) and will not be repeated here except as they relate to the finite element modeling results.

A 3D finite element model for this design was built with the commercial finite element analysis software known as ANSYS using the known dimensions and layer thicknesses for each material (500 nm for the SiNx, 225 nm for the SiO2, and 35 nm for the Pt layers, respectively). To evaluate the microdevice performance and the validity of its associated conduction analysis, a nanowire sample of known thermal conductance was added to the model along with Pt contacts similar to those shown in Figure 3.3(b). To achieve the most realistic simulation possible, the sample of choice was a 56 nm Si nanowire with thermal conductivity set to be that measured by Li et al. (Li, Wu et al. 2003) for a 56 nm diameter VLS Si nanowire in an earlier work. For simplicity, the nanowire was given a square cross section. Images of the finite element model with and without the nanowire sample are shown in Figure 3.4.

Boundary conditions for the finite element simulation consisted of specifying the substrate temperature at the ends of the supporting beams and an appropriate volumetric heating rate for the serpentine heater and the two supporting beams by which the DC heating current to the serpentine heater would be supplied in experiment. For simulations in which radiation effects were considered, there are additional temperature-dependent heat flux boundary conditions which depend on the emissive properties of the device materials, the number of radiation shields present (for the standard cryostat setup, this value is 1), and the specific cryostat geometry. The calculation of radiation heat losses
for the experimental setup used by the Shi group follows from basic radiation analysis similar to Example 13.5 in Incropera and Dewitt (Incropera and Dewitt 2002).

When mounted on the copper cold finger of the cryostat, the front of the microdevice faces the radiation shield mounted between the cold finger and the exterior cryostat wall. The flux of heat lost via radiation from the device’s front face $q_{rad, front}$ can be written as

$$q_{rad, front} = \varepsilon_d \left( \sigma_{SB} T - J_{shield,i} \right)$$

where $\varepsilon_d$ is the device emissivity (SiO$_2$ for the front, SiN$_x$ for the back), $\sigma_{SB}$ is the Stefan-Bolzmann constant, $T$ is the local temperature of the device, and $J_{shield,i}$ is the radiosity of the radiation shield’s inner surface. Since the area of the microdevice is many orders of magnitude smaller than the area of the cold finger, the shield’s temperature is dependent on the temperature, area, and surface emissivity of the cold finger rather than the microdevice. The radiosity of the shield’s inner surface is then given by

$$J_{shield,i} = E_{b, finger} - E_{b, outer} \left( \frac{1 - \varepsilon_{finger}}{\varepsilon_{finger} A_{finger}} + \frac{1}{A_{finger}} \right)$$

where $E_{b, finger}$ and $E_{b, outer}$ are the blackbody radiation of the cold finger and outer cryostat wall, respectively, $\varepsilon_{finger}$, $\varepsilon_{outer}$, and $\varepsilon_{shield}$ are the surface emissivities of the cold finger, outer cryostat wall, and radiation shield, respectively, and $A_{finger}$, $A_{outer}$, and $A_{shield}$ are the surface areas of the cold finger, outer cryostat wall, and radiation shield, respectively. The temperature of the outer cryostat wall is 300 K while the cold finger temperature is specified and assumed uniform. Combining Equations 3.18 and 3.19 gives an analytical
expression for the heat flux from the front surface as a function of the local device temperature $T$ which can be used as a boundary condition within the ANSYS simulation.

Similarly, for the backside of the microdevice which faces the etched silicon facets and Au-coated chip carrier, the radiative heat flux is expressed as

$$ q_{\text{rad,back}} = \varepsilon_d (\sigma_{\text{SB}} T - J_{\text{Si}}) $$

(3.20)

where $J_{\text{Si}}$ is the radiosity of the etch pit, excluding the low emissivity Au layer. Using a pseudo-surface approach to model the etch pit, $J_{\text{Si}}$ can be determined from

$$ J_{\text{Si}} = E_{\text{b, Si}} - J_{\text{shield, Si}} \left( \frac{1 - \varepsilon_{\text{Si, SI}}}{\varepsilon_{\text{Si}}} \right) $$

(3.21)

where $E_{\text{b, Si}}$, $\varepsilon_{\text{Si}}$, and $A_{\text{Si}}$ are the blackbody radiation, emissivity, and surface area from the Si etch pit, respectively, and $A_{\text{pseudo}}$ is the area of the pseudo-surface over the etch pit opening facing the radiation shield. Similar to the front face of the microdevice, the analytical expression obtained by combining Equation 3.20 and Equation 3.21 gives the heat flux from the back surface as a function of the local device temperature $T$ which and serves as a second radiation boundary condition within the ANSYS simulation.
Figure 3.4: 3D ANSYS finite element model of the serpentine heater device. (a) Full view of the suspended microdevice with 400 µm long beams supporting the two membranes. (b) Detail of the membrane region with the SiO₂ layer removed, revealing the serpentine Pt pattern underneath. (c) The membrane region with the oxide layer and suspended nanowire sample shown. (d) Isometric view of the membrane region. (e) Close-up of the nanowire region showing both the nanowire and the four Pt contacts.
Thermal conductivity values of the constituent materials were taken from literature for amorphous SiO$_2$ (Cahill 1990), amorphous SiN$_x$ from similar processing conditions (Mastrangelo, Tai et al. 1990; Zink and Hellman 2004; Sultan, Avery et al. 2009), and thin film Pt (Zhang, Xie et al. 2005; Zhang, Cao et al. 2006). When these material properties were used to calculate the thermal conductance of a supporting beam of the same dimensions and material thicknesses as in the actual suspended device, the calculated beam thermal conductance was in good agreement with the range of beam conductance values typically measured for the actual suspended microdevices. For each of the simulated substrate temperatures (300 K, 450 K, and 600 K), the maximum temperature rise in the converged simulations did not exceed 25 K above the specified substrate temperature. Thus, the temperature dependence of the thermal conductivity of the materials was ignored within each individual simulation. However, temperature dependence of the thermal conductivities was taken into account between each of the simulated substrate temperatures, respectively, such that $\kappa(300 \text{ K}) \neq \kappa(450 \text{ K}) \neq \kappa(600 \text{ K})$ for the device materials.

The simulation itself does not return thermal conductance values directly. Rather, for a specified volumetric heating the temperature at each node in the domain is calculated according to the prescribed boundary conditions and finite element heat transfer methods inherent to ANSYS. To obtain the thermal conductance of the beams and nanowire sample “measured” in the simulation, the nodal temperatures associated with ONLY the serpentine resistance thermometers were retained. In the actual experiment, the electrical resistances of the serpentine coils are measured and knowledge of their change in resistance with temperature used to determine the temperature rise in each membrane during measurement. To follow this same approach in the case of the ANSYS simulation, the nodal temperatures for each of the respective serpentine
resistance thermometers were averaged, thus giving a temperature rise \( \Delta T_H \) for the heating membrane and a temperature rise \( \Delta T_S \) for the sensing membrane. These were then used along with the volumetric heating rates (known in the actual experiment from the measured current and voltage, specified by the user in the ANSYS simulation) in the conduction analysis of the device (Shi, Li et al. 2003; Yu, Saha et al. 2006) to obtain the thermal conductance of the supporting beams and the suspended sample. From this analysis, the thermal conductance of the supporting beams \( G_b = \frac{(Q_H + Q_L)}{\Delta T_H + \Delta T_S} \) and the thermal conductance of the sample \( G_s = G_b \Delta T_S / (\Delta T_H - \Delta T_S) \) were determined from the obtained temperature rises \( \Delta T_H \) and \( \Delta T_S \) and the heat \( Q_H \) and \( Q_L \) generated in the serpentine heater and each of the DC current-carrying legs, respectively. To simulate the actual measurement, three heating rates (and, as a result, three temperature gradients) were simulated and the “measured” thermal conductance of the beams and of the nanowire sample were taken from the slope of the three simulations. This closely follows the measurement analysis procedure used for these types of experiments (Shi, Li et al. 2003; Yu, Saha et al. 2006). The applied volumetric heating values were adjusted such that the resulting temperature differences between the two membranes were similar to those used in the actual measurements.

Representative temperature contour results are shown in Figure 3.5. In the conduction analysis for this device, one of the assumptions used is that the temperature on each membrane is isothermal. The temperature distribution results of the simulation showed that the temperature uniformity on each membrane is quite high, validating the assumption. In addition, the beam and sample thermal conductance values obtained from the simulated measurement are all within \( \sim 1\% \) of the known values as shown in Table II. This suggests that the conduction analysis and its associated assumptions work well for describing the thermal measurement behavior of this particular device design. As a
As a result, the thermal and thermoelectric transport properties measured using this device design are likely more subject to the experimental uncertainties rather than analysis or device design errors.

Figure 3.5: Temperature contours of the membrane region from the finite element analysis of the serpentine heater device. Inset: Temperature contours of the entire finite element model.
Table II. Percent error of the finite element simulation results of the serpentine heater microdevice as compared to the known thermal conductance values of the beams ($G_b$) and sample ($G_s$) at various substrate temperatures ($T_{\text{sub}}$). Results are shown with and without radiation effects included in the simulation.

<table>
<thead>
<tr>
<th>$T_{\text{sub}}$ (K)</th>
<th>Radiation?</th>
<th>% Error $G_b$</th>
<th>% Error $G_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>No</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>450</td>
<td>No</td>
<td>0.8</td>
<td>-0.1</td>
</tr>
<tr>
<td>600</td>
<td>No</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>300</td>
<td>Yes</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>450</td>
<td>Yes</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>600</td>
<td>Yes</td>
<td>1.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

There remains one additional important finding from the finite element simulation of this suspended microdevice design that is not readily apparent from the summarized results of Table II. As mentioned previously, in the actual measurement the change in electrical resistance of the serpentine resistance thermometers is measured and translated to temperature rise using knowledge of their respective change in resistance with temperature. This change in resistance with temperature is determined by measuring the electrical resistance of the serpentine coils at zero DC voltage at each measurement temperature. To perform this calibration, the temperature of the serpentine coil during this initial resistance measurement must be known. It must then be assumed that the temperature of the serpentine coils at zero DC voltage is the same as that reported by the silicon diode which controls the cryostat equilibration. This assumption can be checked by performing the radiation-included finite element simulations for the device with zero heat generation. At 300 K, the temperature of the entire device remains a uniform 300 K as is expected since the outside of the cryostat is at 300 K as well. However, as shown in Figure 3.6, at 450 K and 600 K the radiation loss from the membranes to the 300 K
exterior through the single radiation shield combined with the thermal resistance offered by the long, thin beams result in serpentine temperatures that can be significantly below that of the substrate (~7.5 K difference at 450 K, ~21 K difference at 600K). In these cases, using the diode output temperature to calibrate the resistance versus temperature relationship of the serpentes can lead to inaccurate translation of the measured resistance changes to temperature rise and, as a result, inaccurate thermal conductance values. This effect is not apparent in the finite element simulations because the temperature is calculated directly and is a known quantity, thus acting as if the resistance changes with temperature were known exactly. Since the associated conduction analysis relies only on knowledge of the changes in serpentine temperatures and not the absolute temperatures, the conduction analysis of the finite element simulation results still return accurate values of the beam and sample thermal conductance despite reduced membrane temperatures from radiation losses. However, in terms of improving the overall measurement method, this result highlighted the need to minimize radiation losses from the suspended device to the environment by having radiation shielding present at the substrate temperature rather than at the ambient temperature. In part due to this finding, the cryostat setup used by the Shi group was modified to include an additional radiation shield immediately adjacent to the sample space and connected to the cold finger of the cryostat such that its temperature would be much closer to the substrate temperature than the secondary radiation shield or the cryostat exterior.
Figure 3.6: Temperature contours of the finite element model with no heat generation and radiation effects included at substrate temperatures of (a) 450 K and (b) 600 K.
Line Heater Device

Following the simulation methodology described in the previous section, an alternative suspended microdevice design developed by the Shi group which uses a line heater rather than a serpentine heater was studied. This device features shorter supporting beams and no SiO$_2$ layer. SEM images of the device design under investigation are shown in Figure 3.7.

![Figure 3.7: Suspended microdevice with a line heater developed by the Shi group for thermal and thermoelectric characterization of nanostructures. (a) Full view of the suspended region. Details of the suspended membrane area are shown in (b), where the bright rectangles at the sample-electrode intersections are amorphous carbon-Pt contacts from beam-induced deposition used to improve the electrical and/or thermal contact resistances.](image)

In this design the average change in electrical resistance (and, hence, average change in temperature) of the heating and sensing line are measured during the experiment. The change in temperature at the midpoint (membrane area) of each of these
Pt lines is then found from the measured average temperature rise using an analytical expression relating the two obtained from conduction analysis. For the sensing line without Joule heating, this relation is simply

\[ \Delta T_s = \frac{\Delta \bar{T}_s}{1 - \frac{\chi}{2}} \] (3.22)

where \( \Delta T_s \) is the temperature rise at the midpoint of the sensing line, \( \Delta \bar{T}_s \) is the average temperature rise of the sensor line as measured in the experiment, and \( \chi = \frac{2L_{beam}}{2L_{beam} + L_{membrane}} \). Here, \( L_{beam} \) is the length of one beam (200 \( \mu \)m) and \( L_{membrane} \) is the length of the membrane parallel to the beams (13 \( \mu \)m). For the heating line, the relation between the average temperature rise and the midpoint temperature rise is given by

\[ \Delta T_H = \frac{\Delta \bar{T}_H}{1 - \frac{7}{24} \chi - \frac{12 \frac{1}{5} \chi}{(2 - \chi)\left(\frac{17}{10} + \frac{12 \frac{1}{5} \chi}{\chi}\right)}} \] (3.23)

where \( \Delta T_H \) is the temperature rise at the midpoint of the heater line and \( \Delta \bar{T}_H \) is the average temperature rise of the heater line as measured in the experiment. In addition to the two cases of simulations with and without radiation losses, device designs with and without connecting bars between the supporting beams were considered in order to investigate their influence on the device performance. For the device design without connecting bars, the relations between the midpoint temperatures and the average line temperatures differ from those presented in Equations 3.22 and 3.23. The focus,
however, will remain on the design with connecting bars since it was actually fabricated and is generally more feasible in terms of ease of use.

Images of the finite element models built in ANSYS are shown in Figure 3.8. Specified substrate temperature, volumetric heat generation within the heater line, and radiation heat flux boundary conditions were used similar to the description given in the previous section, as was the same nanowire sample of known thermal conductance. After each simulation reached convergence, the nodal temperatures associated with the heater and sensor lines were extracted and their respective averages used in the conduction analysis to obtain the midpoint temperature rise values $\Delta T_H$ and $\Delta T_S$. The temperature rise values were then used in the same conduction analysis as used in the previous section (Shi, Li et al. 2003; Yu, Saha et al. 2006) with $Q_H = 0$ to obtain the beam and sample thermal conductance values.

Figure 3.8: 3D ANSYS finite element model of the line heater device. (a) Full view. (b) Detail of the membrane region. (c) Isometric view of the membrane.
Representative temperature contour results are shown in Figure 3.9. As shown in Table III, the beam and sample thermal conductance values obtained from the simulated measurements were all within ~2% of the known values for the device design with connecting bars and within ~5% of the known values for the device design without connecting bars. This difference between the two designs stems from the assumption of temperature uniformity on the membrane used in the conduction analysis. As can be seen in the temperature contours of Figure 3.9, the connecting bars help ensure this condition occurs by spreading the heat more uniformly between the supporting beams. The results suggest that the conduction analysis and its associated assumptions work well for describing the thermal measurement behavior of the line heater device design with connecting bars. As a result, the thermal and thermoelectric transport properties measured using this device design are likely more subject to the experimental uncertainties rather than analysis or device design errors.

Table III. Percent error of the finite element simulation results of the line heater microdevice as compared to the known thermal conductance values of the beams ($G_b$) and sample ($G_s$) at various substrate temperatures ($T_{sub}$). Results are shown with and without radiation effects included in the simulation.

<table>
<thead>
<tr>
<th>Device</th>
<th>$T_{sub}$ (K)</th>
<th>Radiation?</th>
<th>% Error $G_b$</th>
<th>% Error $G_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Heater w/ Bars</td>
<td>300</td>
<td>No</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Line Heater w/ Bars</td>
<td>450</td>
<td>No</td>
<td>1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Line Heater w/ Bars</td>
<td>600</td>
<td>No</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Line Heater w/ Bars</td>
<td>300</td>
<td>Yes</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Line Heater w/ Bars</td>
<td>450</td>
<td>Yes</td>
<td>1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Line Heater w/ Bars</td>
<td>600</td>
<td>Yes</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Line Heater w/o Bars</td>
<td>300</td>
<td>No</td>
<td>2.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Line Heater w/o Bars</td>
<td>300</td>
<td>Yes</td>
<td>2.3</td>
<td>4.3</td>
</tr>
</tbody>
</table>
Figure 3.9: Temperature contours from the finite element analysis of the line heater device. (a) Membrane region of the line heater device with connecting bars. (b) Expanded view of the line heater device with connecting bars. (c) Membrane region of the line heater device without connecting bars. (a) Expanded view of the line heater device without connecting bars. All results have radiation effects included.

Radiation losses were found to pose much less of a problem for this suspended device design as compared to the serpentine heater device in the previous section. Even at 600 K the membrane temperature differed from the substrate temperature by less than 1 K. This improvement is due to the lack of an oxide layer such that the majority of the
device facing the cryostat exterior is covered by the Pt lines. These Pt features have much lower emissivity than the SiO$_2$ present on the front of the serpentine device. In this way the Pt lines effectively shield the front face of the device except for the exposed SiN$_x$ portions of the membranes from the cryostat exterior at ambient temperature. However, if the front of the line heater device did possess an oxide layer, the radiation error should in fact be larger than observed for the serpentine heater design. This is due to the line heater design’s reliance on measuring the average temperature rise of the resistance thermometers rather than the actual temperature rise of the membrane regions as in the serpentine device.

**Supporting Bridge Device – Design 1**

The microdevice designs studied in the previous two sections utilized a sample suspended between two membranes. However, in some cases it is necessary or desirable to not have the sample suspended but rather supported on a bridge between the heating and sensing areas of the device. The basic idea behind this approach is to measure the thermal conductance of the bridge both with and without the sample present. The difference between these two measurements is then taken to be the thermal conductance of the sample alone. Besides its obvious exclusion of TEM capabilities, the validity of the bridge technique and its thermal conductance subtraction scheme likely depends on the specific device design through which it is implemented. In this section, finite element analysis of a bridge device as developed by the Heath group at Cal Tech in their investigation of thermoelectric transport of Si nanowires (Boukai, Bunimovich et al. 2008) is presented.

Images of the suspended bridge device used in the Si nanowire work are shown in Figure 3.10 along with the corresponding finite element model. Details of the sample
Figure 3.10: Images of the supporting bridge device Design 1 finite element model. (a) Finite element model with the mesh not shown for clarity. (b) Full view. (c) Close up of the nanowire array (horizontal lines) within the sample area of the bridge. (d) Top-down view of the main measurement area of the finite element model showing the serpentine patterns, four-probe temperature sensors contacting the nanowire array, and the nanowire array itself spanning the supporting bridge region.

preparation, device fabrication, and measurement methods and results can be found elsewhere (Boukai, Bunimovich et al. 2008). The device is entirely comprised of SiO$_2$ and Pt metal lines with a sample space for either a thin film or nanowire array in the
middle of the bridge area. The measurement principle is similar to that employed in the suspended devices considered previously and can be found in the supplemental information of Boukai et al. (Boukai, Bunimovich et al. 2008).

Using the concept of a simulated experiment, finite element simulations were performed for a variety of sample types as well as a device with no sample present, i.e. the SiO$_2$ bridge only. Upon convergence, the obtained nodal temperatures from the inner four-probe temperature sensors were obtained and the data processed according to the conduction analysis used by Boukai et al. for this device design (Boukai, Bunimovich et al. 2008). This analysis results in the same expressions for $G_b$ and $G_S$ as described for the serpentine heater device with $Q_L = 0$. The obtained thermal conductance from the empty bridge simulation was then subtracted from the thermal conductance obtained from the bridge with sample simulation with the difference taken as the sample thermal conductance as in the original experimental work. As in the previous two sections, the simulation was run for three different heating rates and the obtained thermal conductance values for the beams and the sample space taken from the associated slopes. However, due to the design complexity and cryostat-dependent parameters, radiation effects were not considered for this device design. This reduces the motivation to simulate high temperature measurements such that all simulations for this device design were performed at a substrate temperature of 300 K.

The simulated samples span a large range of thermal conductance. The simulated samples include a solid 35 nm Si thin film as measured in the work of Boukai et al. (Boukai, Bunimovich et al. 2008) both with bulk thermal conductivity of 150 W/m-K (Glassbrenner and Slack 1964) and the ~35 nm thin film value of 35 W/m-K approximated from measurements in the literature (Liu and Asheghi 2005). Nanowire arrays similar to those measured in the work of Boukai et al. (Boukai, Bunimovich et al.
were also considered using the 56 nm and 22 nm diameter Si nanowires with thermal conductivity values as measured by Li et al. (Li, Wu et al. 2003) of 25.56 W/m-K and 6.78 W/m-K, respectively. In the final simulation, the thermal conductivity of the 22 nm diameter nanowire array was set to the actual value measured in the work of Boukai et al. (Boukai, Bunimovich et al. 2008) of 3.5 W/m-K.

The numerical results for each simulated sample are shown in Table IV, while representative temperature contours of the main measurement region are shown in Figure 3.11. As shown in Table IV, the simulated samples with the highest thermal conductance values (Si thin film with bulk thermal conductivity, 56 nm diameter nanowire array) also gave the largest errors of ~-25 % and ~-11%, respectively. The errors were ~6 % or less for the two lowest thermal conductance samples simulated, namely the two 22 nm diameter nanowire array cases.

This device behavior can be best understood by examining the representative temperature contours shown in Figure 3.11. Because the sample space is localized in the middle of the bridge rather than being uniform over the bridge width, a high thermal conductance resulted in a 2D temperature distribution over the measurement area (Figure 3.11(a) and (b)). By contrast, the temperature distribution obtained in simulation of the bare SiO$_2$ bridge (not shown) showed a quasi-1D temperature distribution across the device. The non-1D temperature gradient when a localized, high conductance sample is present affects the average temperature of the four-probe resistance thermometer lines contacting the sample, thereby leading to the large errors associated with this condition. The simulation results for the low thermal conductance samples, on the other hand, showed a quasi-1D temperature gradient across the measurement area (Figure 3.11(c) and (d)) similar to that observed for the SiO$_2$-only case in which the thermal conductance is uniform across the width of the bridge. This suggests that in order for the current bridge
design to be useful in the measurement of large thermal conductance samples, the samples should be made to span the width of the supporting bridge to encourage a uniform, 1D temperature gradient and not be localized in the middle.

Table IV. Percent error of the finite element simulation results of supporting bridge microdevice Design 1 as compared to the known thermal conductance values of the beams \( (G_b) \) and sample \( (G_s) \) for several simulated samples. All simulations were for a substrate temperature of 300 K and no radiation effects were included.

<table>
<thead>
<tr>
<th>Device</th>
<th>% Error ( G_b )</th>
<th>% Error ( G_s )</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridge w/o Film</td>
<td>0.8</td>
<td>0.1</td>
<td>35 nm film</td>
</tr>
<tr>
<td>Bridge w/ Film</td>
<td>-0.4</td>
<td>-17.1</td>
<td>( \kappa=150 \text{ W/m-K} )</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>-25.1</td>
<td></td>
</tr>
<tr>
<td>Bridge w/o Film</td>
<td>0.8</td>
<td>0.1</td>
<td>35 nm film</td>
</tr>
<tr>
<td>Bridge w/ Film</td>
<td>-0.2</td>
<td>-2.9</td>
<td>( \kappa=35 \text{ W/m-K} )</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>-9.9</td>
<td></td>
</tr>
<tr>
<td>Bridge w/o Nanowires</td>
<td>-0.2</td>
<td>0.4</td>
<td>56 nm nanowire array</td>
</tr>
<tr>
<td>Bridge w/ Nanowires</td>
<td>-1.0</td>
<td>-5.0</td>
<td>( \kappa=25.56 \text{ W/m-K} )</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>-11.4</td>
<td></td>
</tr>
<tr>
<td>Bridge w/o Nanowires</td>
<td>-1.2</td>
<td>10.7</td>
<td>22 nm nanowire array</td>
</tr>
<tr>
<td>Bridge w/ Nanowires</td>
<td>-1.2</td>
<td>9.7</td>
<td>( \kappa=6.78 \text{ W/m-K} )</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>-1.5</td>
<td></td>
</tr>
<tr>
<td>Bridge w/o Nanowires</td>
<td>-1.2</td>
<td>10.7</td>
<td>22 nm nanowire array</td>
</tr>
<tr>
<td>Bridge w/ Nanowires</td>
<td>-1.2</td>
<td>6.1</td>
<td>( \kappa=3.50 \text{ W/m-K} )</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

Though the measurement of low thermal conductance samples avoids this issue, a separate complication occurs in this case. If the sample thermal conductance is small then the thermal conductance values from the sample-on-bridge measurement and the bare bridge measurement would be very similar. The subsequent subtraction to obtain the sample thermal conductance would involve subtracting two very similar numbers. Given the presence of experimental uncertainty of a few percent in both measurements,
this type of subtraction has the potential to lead to high relative error in the resulting sample thermal conductance values. This issue would also be helped by extending the sample space to be the same width as the bridge, thereby increasing the sample thermal conductance.

Figure 3.11: Temperature contours of supporting bridge Design 1 for (a) 35 nm solid thin film with bulk thermal conductivity, (b) 56 nm diameter nanowire array, (c) 22 nm diameter nanowire array with $\kappa = 6.78$ W/m-K, and (d) 22 nm diameter nanowire array with $\kappa = 3.5$ W/m-K.
Supporting Bridge Device – Design 2

A more simplistic design using the supporting bridge approach was employed in the thermal conductivity measurement of SiO$_2$-supported single layer graphene described in Chapter 2. The measurement analysis for this device is similar to that of the line heater device discussed previously. Briefly, the measured average temperature rise of the four resistance thermometers are used along with conduction analysis to find the midpoint temperature changes. These temperature rises are then used to determine the thermal conductance of the sample and bridge from an energy conservation analysis. Full details of the experiment and its associated conduction analysis can be found elsewhere (Seol, Jo et al. 2010). Finite element simulation of this device design was used as a means to validate these analytical expressions.

The supporting bridge device developed by the Shi group is shown in Figure 3.12 along with its associated finite element model. The device is comprised of patterned Au lines on SiO$_2$. The central measurement region consists of the single layer graphene sample supported by a SiO$_2$ bridge of the same width and length. The thermal conductivity of the thin film Au used in the finite element simulation was determined from the measured electrical resistivity of the actual device and the Lorenz number for Au (Ashcroft and Mermin 1976) to be 189 W/m-K at 300 K, several times larger than the 30 W/m-K thermal conductivity at the same temperature of the thin film Pt (Zhang, Xie et al. 2005; Zhang, Cao et al. 2006) used in the preceding device designs. The sample in this case is single layer graphene with a thickness of 0.335 nm which was found to have a room temperature thermal conductivity of $\sim$535 W/m-K in the oxide-supported state (Seol, Jo et al. 2010). If the graphene layer were modeled to scale in the finite element model, achieving a reliable mesh would require a prohibitively large number of nodes not allowed within the ANSYS software. Instead, the graphene is represented by a thin solid
Figure 3.12: Supporting bridge microdevice design developed by the Shi group for measurement of SiO$_2$-supported single layer graphene (SLG). (a) Schematic of the device and its constituent materials. (b) Close up of the bridge-supported film area of the finite element model. (c). Full view SEM image of the fabricated device design. (d) Full view of the finite element model. (e) Detail of the supported graphene region of the fabricated...

A film of equivalent thermal conductance achieved by multiplying (dividing) the thickness (thermal conductivity) by a factor of 100. Using this approach the sample film in the finite element model was assigned a thickness of 33.5 nm and a thermal conductivity of 5.35 W/m-K.

Another point of interest was the effect of thermal contact resistance between the graphene and the device materials on the measured sample thermal conductance. To investigate this, the finite element analysis was performed for the device assuming perfect contacts (no thermal contact resistance) and performed again using thermal contact resistance values from literature. For the graphene-Au interface, a thermal interface conductance of 50 MW/m²-K was used as found between graphite and evaporated Al (Schmidt, Chen et al. 2008). For the graphene-SiO₂ interface, a thermal interface conductance of 83 MW/m²-K was used as found for SiO₂-embedded graphene (Chen, Jang et al. 2009). It should be noted that literature values were used here due to this work predating that done for the Au-supported CVD graphene measurement described in the previous section.

The numerical results of the finite element analyses are summarized in Table V while representative temperature contours are shown in Figure 3.13. As in the previously studied designs, the beam and sample thermal conductance values were determined using
the slope approach from the simulation results obtained with three different heat generation rates. Radiation losses were found to have a negligible effect on the simulation results due to the significant metal coverage on the front face of the device and the relatively high emissivity of the silicon etch pit facing the backside of the device. This silicon pit is at the substrate temperature such that any radiation losses from the front side of the device to the cryostat exterior are compensated and the device remains at the substrate temperature for zero DC heating voltage. The quantitative effect of considering non-perfect thermal interfaces can be seen in the results listed in Table V. For perfect thermal interfaces with zero contact resistance the error in the obtained sample thermal conductance was ~4.5 %, while for literature thermal contact resistances the error was ~4%. The difference in solutions stems from the effect of the thermal interface condition on the temperature uniformity in the bridge region for the inner two resistance thermometer lines. In the associated conduction analysis, the temperature is assumed to be uniform across the bridge region for these lines and equal to the temperature at the beam-bridge interface. The temperature contours in Figure 3.13 reveal a 1D temperature gradient across the supporting bridge region as well as nearly uniform temperatures in the bridge region for the inner two resistance thermometer lines. However, a small degree of nonuniformity not visible in the contours is still present numerically in these regions. The second assumption regarding the bridge-beam interface temperature is also shown in the temperature contours to be slightly inaccurate and also affected by the thermal interface condition. When combined these effects still result in absolute error of less than 5% associated with the use of the conduction analysis; this is below the experimental uncertainty found for the actual measurement.
Figure 3.13: Temperature contours of supporting bridge device Design 2. Results are shown using (a) perfect thermal contacts and (b) thermal contact resistances from literature.
Table V. Percent error of the finite element simulation results of supporting bridge microdevice Design 2 as compared to the known thermal conductance values of the beams ($G_b$) and sample ($G_s$) for several simulated samples. All simulations listed were for a substrate temperature of 300 K and radiation effects were included.

<table>
<thead>
<tr>
<th>Device</th>
<th>% Error $G_b$</th>
<th>% Error $G_s$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridge w/ Film</td>
<td>-1.3</td>
<td>-0.2</td>
<td></td>
</tr>
<tr>
<td>Bridge w/o Film</td>
<td>2.4</td>
<td>1.8</td>
<td>Perfect thermal contacts</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>-4.5</td>
<td></td>
</tr>
<tr>
<td>Bridge w/ Film</td>
<td>-0.9</td>
<td>2.5</td>
<td>Literature thermal contact</td>
</tr>
<tr>
<td>Bridge w/o Film</td>
<td>2.4</td>
<td>1.8</td>
<td>contact resistances</td>
</tr>
<tr>
<td>Bridge - Subtracted</td>
<td>-</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION

This chapter used analytical and numerical modeling to examine several approaches to measuring the thermal and thermoelectric transport properties of nanostructures. For the Raman measurement of CVD graphene, the analysis helped identify potential sources of error and possible improvements. In addition, the analytical solution to the heat transfer equations enabled the determination of the thermal conductivity and interface conductance of the Au-supported sample region. This illustrates the utility and value of performing rigorous analysis of measurement methods. Likewise, the finite element analyses performed for various suspended microdevice designs did more than simply validate the respective conduction analyses. It also provided an increased qualitative understanding of each design’s thermal behavior especially the temperature distribution in the more complex regions of the devices. This was especially true of the bridge device Design 1 for which the effect of the sample placement and thermal conductance on the measurement accuracy was observed. An
increased understanding of these principles help not just in the analysis of existing device designs but also in the design methodology of future devices for nanoscale energy transport measurements.
Chapter 4: Thermal Conductivity Suppression in Bismuth Nanowires

In this chapter, the measurement and analysis of bismuth nanowire thermal conductivity is presented. The measurements in this work were preformed using the serpentine heater suspended microdevice design developed by the Shi group and analyzed numerically in Chapter 3. It also employs some of the BTE-based modeling approaches presented in Chapter 2 to analyze and discuss the obtained measurement results. This work then serves not just as an investigation of thermal transport in bismuth nanowires but also as a fitting example of how these experimental, numerical, and analytical methods can work together to better understand nanoscale energy transport.

BACKGROUND

The element bismuth (Bi) possesses several interesting physical properties which make it a material of interest to scientists and engineers. These include its long carrier mean free paths (Hartman 1969), small effective mass and long electron wavelength (Heremans and Hansen 1979; Sun, Zhang et al. 1999; Lin, Sun et al. 2000), and semimetal band structure (Gallo, Chandrasekhar et al. 1963; Hartman 1969; Heremans and Hansen 1979; Sun, Zhang et al. 1999; Lin, Sun et al. 2000). The highly anisotropic transport properties (Gallo, Chandrasekhar et al. 1963) that arise from these physical attributes have also been well studied. In particular, Bi-based alloys have been extensively investigated for use in thermoelectric applications. This interest in part stems from the fact that bismuth
possesses the lowest thermal conductivity of all metals except mercury, noting that a low thermal conductivity is desirable for high $ZT$ as discussed in Chapter 1. However, the semimetal band structure present in bulk, pure Bi severely limits its potential as a good thermoelectric material (Liu and Allen 1995; Lin, Sun et al. 2000; Boukai, Xu et al. 2006). A semimetal band structure like that found in bulk Bi consists of a small band overlap between the conduction and valence bands, resulting in nearly equal concentrations of electrons and holes. This in turn causes the electron and hole contributions to the Seebeck coefficient to effectively cancel one another and have a low magnitude (Gallo, Chandrasekhar et al. 1963; Liu and Allen 1995; Lin, Sun et al. 2000; Boukai, Xu et al. 2006). The same effect was discussed in Chapter 2 as a possible cause of the low Seebeck magnitudes observed for Bi$_2$Te$_3$ nanowires. In their investigations of thermoelectric transport in bulk Bi, Gallo et al. (Gallo, Chandrasekhar et al. 1963) postulated that the optimum $ZT$ would occur in a single carrier system with either electrons or holes dominating the transport. They also suggested that such a situation could be realized via doping of Bi with antimony or tellurium (Gallo, Chandrasekhar et al. 1963), an assertion which has been found to be true in the realization of relatively high $ZT$ for Bi-Sb-Te systems (Rowe 1994; Poudel, Hao et al. 2008) and Bi$_2$Te$_3$ (Goldsmid 1964; Rowe 1994). In addition to increasing the magnitude of the Seebeck coefficient, the transition to a single carrier system suppresses the bipolar contribution to the thermal conductivity, thereby further increasing $ZT$ (Gallo, Chandrasekhar et al. 1963).

Interest in thermoelectric transport in Bi was renewed when theoretical investigations of size effects as discussed in Chapter 1 predicted an enhancement in $ZT$ for 1D and 2D Bi and Bi-based nanostructures (Hicks and Dresselhaus 1993; Sun, Zhang
et al. 1999; Lin, Sun et al. 2000; Rabin, Lin et al. 2001). These predictions suggested that when the diameter of a Bi nanowire becomes comparable to or smaller than the long (~50 nm) de Broglie wavelength of electrons, the resulting highly asymmetric electron density of states could enhance the thermoelectric power factor $S^2\sigma$ (Chen and Shakouri 2002). It was also predicted that the conduction/valence band overlap found in bulk Bi should be inversely proportional to the square of the nanowire diameter. Thus, for decreasing nanowire diameter a semimetal-to-semiconductor transition could occur in the band structure (Lin, Sun et al. 2000), thereby making it possible to break the electron-hole symmetry and reap the same thermoelectric benefits described above for single carrier transport achieved by doping.

Besides quantum size effects, classical size effects are expected to greatly influence the transport properties of Bi nanostructures due to the exceptionally long charge carrier mean free paths present in bulk Bi. These mean free paths have been found to be up to ~400 µm for electrons and ~200 µm for holes at 4.2 K and ~100 nm for electrons and holes at room temperature (Hartman 1969; Heremans, Thrush et al. 2000). However, despite the possibility of observing several interesting size effects, the measurement of thermal transport in Bi nanowires had not been reported prior to this work (Moore, Pettes et al. 2009). Moreover, while the reduction in thermal conductivity due to phonon boundary scattering in nanostructures has been actively investigated for some time, there have been few studies regarding classical size effects on the electronic thermal conductivity for nanostructured materials in which thermal transport by charge carriers is significant.
In this work, the thermal conductivities of individual Bi nanowires were measured using a suspended microdevice and the crystal structure-thermal conductivity relationship was studied. Transport models were then used to analyze the data and explore the effects of size confinement, grain boundaries, defects, and impurities on the contributions of phonons, electrons, holes, and bipolar diffusion to Bi nanowire thermal conductivity.

METHODS

Bismuth nanowires were synthesized using the template-assisted vapor deposition method first reported by Heremans et al. (Heremans, Thrush et al. 2000). In this method, bismuth vapor is condensed and solidified within the aligned pores of a template which defines the nanowire geometry. To serve as a template, anodic alumina membranes (AAMs) of tunable pore diameter were grown via a two-step anodization method (Masuda and Satoh 1996; Xu, Piner et al. 2003). Additional AAM templates were obtained commercially from Whatman or Synkera Technologies. Following Bi deposition, the impregnated AAMs were placed in a solution of 2 M sodium hydroxide (NaOH) for 30 minutes, dissolving the ceramic alumina template and releasing individual Bi nanowires into the NaOH. This was followed by repeated dilution and removal with deionized (DI) water until a nanowire solution of neutral pH was achieved. The DI water was then replaced with isopropyl alcohol (IPA) three times to produce a fluidic suspension of individual Bi nanowires in IPA. This low surface tension nanowire suspension was then used for drop casting onto the suspended microdevices to trap individual nanowires for measurement.
Figure 4.1: SEM images of a representative suspended microdevice. (a) Full view of the suspended membranes and supporting beams. (b) Detailed view the suspended membrane region with a Bi nanowire trapped across the gap. (c) Close-up of a Bi nanowire sample with arrows indicating amorphous carbon-Pt contacts from beam-induced deposition used to improve the thermal contact. Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* **106**, 2009, 034310, copyright 2009 American Institute of Physics.

The suspended microdevice shown in Figure 4.1 was used to measure the thermal conductance of individual Bi nanowires bridging the two SiNx membranes. Each membrane consists of two Pt electrodes and a serpentine Pt resistance thermometer.
(PRT), with the PRT region covered in SiO$_2$ to prevent shorting with the nanowire sample. Each membrane is suspended by six SiO$_2$-Pt-SiN$_x$ beams over a through-substrate hole which allows for TEM characterization of the sample following measurement. Correlation of the measured thermal properties with the crystal quality and the growth direction of the nanowire sample is especially important given the highly anisotropic nature of bulk Bi (Gallo, Chandrasekhar et al. 1963).

Electron beam-assisted deposition of carbon-Pt contacts like those visible in Figure 4.1(c) was used to improve the thermal contact between the nanowire and the Pt electrodes but did not result in electrical contact. Previous studies have found that Bi nanowires form a highly stable surface oxide layer in air, making it challenging to achieve ohmic electrical contact (Cronin, Lin et al. 2002; Cronin, Lin et al. 2002).

Thermal conductance measurements of the Bi nanowire samples were conducted under vacuum in a cryostat following the experimental procedures described elsewhere (Shi, Li et al. 2003; Yu, Saha et al. 2006). The same thermal conductance measurement was also performed using a suspended microdevice without a nanowire trapped between the two membranes in order to measure any background signal which might be present due to heating of the substrate, residual gas molecules in the evacuated cryostat, or radiation. For each nanowire sample, the measured background signal was subtracted from measured nanowire thermal conductance at the corresponding temperature. The background signal was found to be at least about one order of magnitude smaller than the thermal conductance values measured for the Bi nanowire samples as shown in Figure 4.2.

The crystal quality and structure of samples NW2, NW3, and NW6 were characterized by TEM following the thermal conductance measurements. The other three nanowire samples were inadvertently broken at the membrane edges when removing the device chip from the ceramic chip carrier, thus making TEM characterization of these samples impossible. Where possible, the total outer diameter and the oxide shell thickness of the Bi nanowires were determined by TEM. For the remaining samples for which TEM was unavailable, the total outer diameter was measured using SEM. A
A summary of the measured Bi nanowire samples including information from TEM characterization is given in Table VI.

As shown in Figure 4.3(a), the high resolution TEM (HRTEM) images and electron diffraction pattern of NW3 indicate that this sample was single crystalline within the \( \sim 2 \, \mu\text{m} \) beam spot and had growth direction perpendicular to the trigonal axis along the \( <1\overline{2}0> \) crystal direction. In contrast, NW2 and NW6 were found to be polycrystalline. Energy-dispersive x-ray spectroscopy (EDX) performed on the suspended TEM samples revealed no impurities present at detectible levels as shown in the representative EDX spectrum shown for NW2 in Figure 4.4.

Figure 4.3: HRTEM images and electron diffraction patterns (insets) of (a) NW3 and (b) NW2. Diffraction patterns were taken using a 2 \( \mu\text{m} \) beam spot. Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* **106**, 2009, 034310, copyright 2009 American Institute of Physics.
Table VI. Summary of the measured Bi nanowire samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outer Diameter (nm)</th>
<th>Suspended Length (µm)</th>
<th>Oxide (nm)</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW1</td>
<td>283</td>
<td>9.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NW2</td>
<td>255</td>
<td>2.56</td>
<td>12-35</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>NW3</td>
<td>232</td>
<td>3.45</td>
<td>10-16</td>
<td>&lt;1 2 0&gt;</td>
</tr>
<tr>
<td>NW4</td>
<td>157</td>
<td>3.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NW5</td>
<td>105</td>
<td>2.22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NW6</td>
<td>74</td>
<td>1.61</td>
<td>3-4</td>
<td>Polycrystalline</td>
</tr>
</tbody>
</table>

Figure 4.4: EDX of NW2 with labeled peaks. The Cu signal is attributed to the TEM sample holder, while the Si peaks are likely from the Si-based microdevice. Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* 106, 2009, 034310, copyright 2009 American Institute of Physics.
RESULTS

Using the measured thermal conductance $G$ of the sample (which includes the thermal contact resistance), the total thermal conductivity $\kappa$ was calculated using $\kappa = GL/A_c$, where $L$ is the length of the suspended nanowire segment and $A_c$ is the cross sectional area calculated using the nanowire diameter $d$. If the cross sectional area for thermal transport is based on the outer nanowire diameter, the resulting cross section includes the native oxide layer and the obtained thermal conductivity would not be that of Bi core alone. This effective total thermal conductivity of the individual oxide-coated bismuth nanowires is shown in Figure 4.5.

![Figure 4.5: Effective total thermal conductivity of individual bismuth nanowires including both the bismuth core and the amorphous oxide shell. Bulk Bi thermal conductivity data perpendicular (a-b plane) and parallel (c axis) to the trigonal crystal direction are taken Gallo et al. (Gallo, Chandrasekhar et al. 1963). Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, J. of Applied Physics 106, 2009, 034310, copyright 2009 American Institute of Physics.](image-url)
To the author’s knowledge, the thermal conductivity of amorphous Bi oxide has not been studied. This necessitated that use of Slack’s minimum thermal conductivity model (Slack 1974) to estimate the thermal conductivity of the oxide shell. The Slack model gives a nearly constant value of 0.34 W/m-K in the measured temperature range between 100 K and 475 K. The oxide shell thickness values given in Table VI were then used along with the estimated oxide thermal conductivity to calculate the thermal conductance of the oxide shell for each sample. For the three samples for which TEM analysis was not possible, an oxide thickness of 10 nm was assumed based on typical oxide thickness values observed by TEM for multiple Bi nanowires. The resulting oxide thermal conductance for each nanowire was then subtracted from the measured thermal conductance similar to what was done for the background signal. This oxide-corrected thermal conductance was used to calculate the thermal conductivity of the Bi core based on the core diameter. It is this thermal conductivity (shown in Figure 4.6) which should be compared to the thermal conductivity of bulk Bi in order to determine the effects of size. The difference between the oxide corrected and oxide-included thermal conductivity is in the range of 9-14% for the measured nanowire samples.

The sample with the largest diameter of 283 nm (NW1) also had the highest thermal conductivity of all samples, though the measured values are still below the thermal conductivity of bulk Bi. The thermal conductivity of NW3 with 232 nm diameter was comparable but somewhat smaller to that of NW1 in the same temperature range. Compared to the bulk Bi, the magnitude and temperature dependence of the thermal conductivity for NW3 was found to be very weak. The thermal conductivity of polycrystalline NW2 with 255 nm diameter was found to be much lower than highly
crystalline NW3 despite their comparable diameters. For the remaining samples with diameters below ~150 nm, the obtained thermal conductivities were greatly reduced compare to bulk Bi and demonstrated no apparent diameter dependence.

Figure 4.6. Oxide-corrected thermal conductivity of the Bi nanowire cores. Bulk values perpendicular (a-b plane) and parallel (c axis) to the trigonal crystal direction taken from Gallo et al. (Gallo, Chandrasekhar et al. 1963). Lines are calculation results as discussed in the text. Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* **106**, 2009, 034310, copyright 2009 American Institute of Physics.
ANALYSIS

Unlike the previously discussed semiconductor nanowire systems for which the total thermal conductivity was dominated by phonons, in semimetallic Bi the contributions of charge carriers to thermal transport cannot be neglected (Gallo, Chandrasekhar et al. 1963). Thus, the separate contributions from each heat carrier (phonons, electrons, and holes) to the total thermal conductivity must be considered in any modeling used to understand the measured nanowire thermal conductivity data. Previously, Uher and Goldsmid (Uher and Goldsmid 1974) showed experimentally using a magnetic field that in bulk Bi phonons are the dominant heat carrier at low temperatures but that the electronic thermal conductivity $\kappa_E=\kappa_e+\kappa_h+\kappa_{eh}$ from charge carriers becomes progressively more important as temperature increases (Uher and Goldsmid 1974), where the thermal conductivities of the charge carriers are as defined in Chapter 1. Their work found that about one third of the total thermal conductivity $\kappa$ is attributable to $\kappa_E$ at the Debye temperature of 120 K (Uher and Goldsmid 1974). Later, Gallo et al. (Gallo, Chandrasekhar et al. 1963) also observed an increasingly important electronic thermal conductivity component with increasing temperature in bulk Bi. They found that at 300 K the electronic thermal conductivity $\kappa_E$ accounted for about 70% of the total thermal conductivity $\kappa$ in the direction perpendicular to the trigonal crystal axis, while the remaining 30% belonged to the phonon thermal conductivity $\kappa_{ph}$ (Gallo, Chandrasekhar et al. 1963).

To better understand the possible mechanisms involved in the observed thermal conductivity reduction and evaluate the relative importance of the various energy carriers
in Bi nanowires, analytical models similar to those used in Chapter 2 were developed that consider thermal transport by phonons, electrons, holes, and bipolar diffusion. This was accomplished by first modeling bulk Bi thermal transport, followed by inclusion of additional boundary scattering and impurity/defect scattering processes for the nanowire transport case and to account for the observed suppression of the thermal conductivity compared to bulk data.

The bulk electronic thermal transport model closely resembles that used by Gallo et al. (Gallo, Chandrasekhar et al. 1963) to study thermal transport in bulk Bi but with more modern information regarding band parameters (Smith 1962; Gallo, Chandrasekhar et al. 1963; Isaacson and Williams 1969; Heremans and Hansen 1979; Lin, Sun et al. 2000) and carrier mobilities (Michenaud and Issi 1972). Due to the lack of Seebeck coefficient data for the measured nanowires, literature bulk Seebeck coefficient data was used instead to determine typical Fermi energies for Bi while assuming parabolic bands and ellipsoidal energy surfaces. Due to the need to consider two-band transport similar to the Bi$_2$Te$_3$ nanowire modeling in Chapter 2, the model must also rely on bulk mobility data for electrons and holes. This reliance restricts the model to temperatures for which there is bulk mobility data available, specifically the temperature range of 77 K to 300 K (Michenaud and Issi 1972). As done previously in the Seebeck coefficient modeling presented Chapter 2, the mean free scattering time $\tau$ is assumed to depend on the carrier energy according to $\tau = r_c E^r$, where $\tau_0$ and $r_c$ are constants. The value of $r_c$ was taken to be -0.5 due to the expected dominance of boundary scattering or acoustic phonon scattering in the case of nanowires and bulk Bi, respectively. This same scattering
exponent value has been successfully used to model bulk Bi in the past (Gallo, Chandrasekhar et al. 1963). Due to the crystal orientation of the highly quality sample NW3, the direction perpendicular to the trigonal axis was chosen as the focus of the model, thus dictating which bulk electron and hole mobility data was used (Michenaud and Issi 1972). The carrier concentrations of electrons and holes have been shown to be almost equal for bulk Bi (Gallo, Chandrasekhar et al. 1963; Liu and Allen 1995; Lin, Sun et al. 2000; Boukai, Xu et al. 2006) as well as thick films (Hoffman, Meyer et al. 1993). This is expected from the semimetal band structure of Bi and was reproduced in the model as shown in Figure 4.7 by the agreement between the bulk Bi modeling results and the measured bulk values of $S$ and $\sigma$. By using bulk band parameters and a 3D density of states in the Seebeck modeling, the model is generally valid for temperatures above 100 K and nanowire diameters larger than about 75 nm where quantum size effects and the associated semimetal-to-semiconductor transition are not expected to be significant or imminent (Lin, Sun et al. 2000).

Using bulk mobility data (Michenaud and Issi 1972) and the Fermi energies determined from the bulk Seebeck coefficient data (Gallo, Chandrasekhar et al. 1963), the electronic thermal conductivity $\kappa_E$ was calculated using (Gallo, Miller et al. 1962; Gallo, Chandrasekhar et al. 1963)

$$\kappa_E = T \left( \frac{k_B}{e} \right)^2 \left[ \gamma(\zeta_e) n e \mu_e + \gamma(\zeta_h) p e \mu_h \right] + e T \left( \frac{n \mu_e p \mu_h}{n \mu_e + p \mu_h} \right) (S_h - S_e)^2$$

(4.1)

where the function $\gamma(\zeta)$ is given by
\[ \gamma(\zeta) = \frac{(r_e + 7/2)F_{r_e+5/2}(\zeta)}{(r_e + 3/2)F_{r_e+3/2}(\zeta)} - \left[ \frac{(r_e + 5/2)F_{r_e+3/2}(\zeta)}{(r_e + 3/2)F_{r_e+1/2}(\zeta)} \right]^2 \] (4.2)

and \( \zeta \) refers to either the electron or hole reduced Fermi energy according the appropriate subscript in Equation 4.1. For these equations, \( F_y(\zeta) = \int_0^{\zeta} \frac{x^y}{e^{(x-\zeta)} + 1} \) is the Fermi-Dirac integral of order \( y \) and all symbols are consistent with the definitions stated previously in Chapter 2.

Figure 4.7: Bulk Seebeck coefficient \( S \) and electrical resistivity \( \rho \) for bismuth perpendicular to the trigonal direction. Lines are from the analytical model, while data points are from Gallo et al. (Gallo, Chandrasekhar et al. 1963). Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, J. of Applied Physics 106, 2009, 034310, copyright 2009 American Institute of Physics.

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Physically, the first and second terms in the bracket of Equation 4.1 represent the electron thermal conductivity $\kappa_e$ and the hole thermal conductivity $\kappa_h$ contributions, respectively. The final term on the right hand side of Equation 4.1 is the bipolar diffusion contribution to the thermal conductivity $\kappa_{eh}$ which is only significant in two-carrier systems.

The bulk phonon thermal conductivity $\kappa_{ph}$ was obtained by subtracting the bulk electronic thermal conductivity $\kappa_E$ values calculated from Equations 4.1 and 4.2 from the experimental values of Gallo et al. (Gallo, Chandrasekhar et al. 1963) for the bulk total thermal conductivity, i.e. $\kappa_{ph} = \kappa - \kappa_E$. The resulting bulk $\kappa_{ph}$ as a function of temperature was modeled using the modified Callaway method developed by Morelli, Heremans, and Slack (Morelli, Heremans et al. 2002), hereafter referred to as the MHS model for brevity. This model makes use of phonon dispersion curves to determine the appropriate limit of integration for each branch as well as reduce the dependence on fitting parameter as compared to the traditional Callaway model (Callaway 1959). Using the bulk phonon dispersion for Bi (Yarnell, Warren et al. 1964; Murray, Fahy et al. 2007), the calculated bulk $\kappa_{ph}$ from the MHS model was found to be in good agreement with the discrete $\kappa_{ph}$ values obtained from the subtraction mentioned above. Both the MHS results and the discrete $\kappa_{ph}$ values are shown in Figure 4.8 along with the phonon thermal conductivity estimated by Gallo et al. (Gallo, Chandrasekhar et al. 1963). From the above bulk Bi thermal conductivity model, the calculated values for bulk total thermal conductivity $\kappa$ as well as the constituent thermal conductivities of phonons, electrons, holes, and bipolar diffusion were obtained and are plotted in Figure 4.9 along with the experimental data of Gallo et al. (Gallo, Chandrasekhar et al. 1963) for bulk Bi.
Figure 4.8: Bulk phonon thermal conductivity perpendicular to the trigonal direction as determined by the author’s modeling and that of Gallo et al. (Gallo, Chandrasekhar et al. 1963). Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* **106**, 2009, 034310, copyright 2009 American Institute of Physics.

With the model calibrated and validated using bulk Bi parameters, the focus shifted to adapting it for describing nanowire thermal transport. The resulting nanowire model is essentially the same as that described above for bulk Bi above but with the addition of charge carrier boundary scattering mobilities and diffuse phonon boundary scattering. The charge carrier surface specularity, impurity concentration $c$, and impurity type are the adjustable parameters within the model for the fitting the experimental thermal conductivity data of NW3. This modified nanowire model is described in detail in the following paragraphs.
Figure 4.9: Calculated total thermal conductivity $\kappa$ of bulk Bi perpendicular to the trigonal crystal axis including the individual contributions of phonons ($\kappa_{ph}$), electrons ($\kappa_e$), holes ($\kappa_h$), and bipolar diffusion ($\kappa_{eh}$). Experimental values taken from Gallo et al. (Gallo, Chandrasekhar et al. 1963). Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, J. of Applied Physics 106, 2009, 034310, copyright 2009 American Institute of Physics.

As in the bulk Bi model, the nanowire phonon thermal conductivity $\kappa_{ph,NW}$ was also calculated using the MHS model with the bulk Bi phonon dispersion relation (Yarnell, Warren et al. 1964; Murray, Fahy et al. 2007). Bulk phonon dispersion is expected to be valid due to the much larger size of the nanowire diameter as compared to the typical dominant phonon wavelength. In addition, evidence was found in literature
that suggests that the sound velocity of acoustic phonons in 200 nm Bi nanowires is similar to that for bulk polycrystalline Bi (Kolomenskii, Jerebtsov et al. 2008), further supporting the use of a bulk dispersion relation. The boundary scattering mean free time \( \tau_{ph,B} \) for a given phonon mode in the nanowire model was obtained from

\[
\tau_{ph,B}^{-1} = \frac{1}{l_{ph,B}} = \frac{v}{l_{ph,B}},
\]

where \( l_{ph,B} \) is the phonon boundary scattering mean free path and \( v \) is the phonon velocity for either the longitudinal or transverse phonon mode as determined from the dispersion relation (Morelli, Heremans et al. 2002). For a nanowire with diameter \( d \), the value of \( l_{ph,B} \) was dependent on the phonon surface specularity \( p_{ph} \) as in Equation 2.59. Using this model, the \( \kappa_{ph} \) of a single-crystal Bi nanowire with the same growth direction and core diameter as NW3 was calculated for the two limiting cases of \( p_{ph} = 0 \) and \( p_{ph} = 1 \). The results are shown in Figure 4.10 along with NW3’s experimental data. The calculated \( \kappa_{ph} \) for the diffuse surface limit \( p_{ph} = 0 \) was only moderately reduced from the specular surface (bulk) result. This result indicated that the nanowire core diameter of 219 nm did not significantly limit the phonon mean free path. In comparison, the bulk phonon mean free path for Bi was calculated to be \(~150\) nm at 300 K based on the empirical relation reported by White and Woods (White and Woods 1958). Compared to bulk Bi, the measured total thermal conductivity \( \kappa \) of NW3 was found to be three times smaller than the lattice thermal conductivity \( \kappa_{ph} \) calculated for bulk Bi at the lowest measurement temperature of 100 K. In addition, the measured \( \kappa \) of NW3 was also lower than the calculated \( \kappa_{ph} \) for the diffuse surface case below 225 K. The above results indicated that the reduction in nanowire thermal conductivity from bulk values could not be explained by diffuse phonon scattering from the nanowire surface alone.
Figure 4.10: Comparison of the measured total thermal conductivity $\kappa$ of NW3 with the calculated phonon thermal conductivity $\kappa_{ph}$ for diffuse and specular surface scattering. Reproduced with permission from A. L. Moore, M. T. Pettes, F. Zhou, L. Shi, *J. of Applied Physics* **106**, 2009, 034310, copyright 2009 American Institute of Physics.

Thermal contact resistance was studied as a possible cause for the measured $\kappa$ being below the calculated $\kappa_{ph}$ for a diffuse nanowire surface. The lack of four-probe electrical contact to the nanowire samples prevented the use of an experimental method by which the thermal contact resistance of the nanowires could be determined directly (Mavrokefalos, Pettes et al. 2007; Zhou, Szczech et al. 2007). However, for the CrSi$_2$ nanowires in Chapter 2 with Pt-C contacts similar to those used in this work, the thermal contact resistance was found to be less than 10% of the total measured thermal resistance.
In lieu of direct measurement, the thermal contact resistance $R_C$ for NW3 was estimated using the approach of Yu et al. (Yu, Saha et al. 2006) as

$$R_C = \sum_{j=1}^{2} \left[ \frac{\kappa A_c}{R_c / b} \tanh \left( \frac{L_{c,j}}{\sqrt{\kappa A_c R_c / b}} \right) \right]^{-1}$$

(4.3)

where $L_{c,1}$ and $L_{c,2}$ are the left and right contact lengths for the nanowire sections in contact with the membrane, $\kappa$ is the thermal conductivity of the Bi nanowire sample, $A_c$ is the cross-sectional area of the nanowire, $b = \pi d$ is the contact width between the nanowire with diameter $d$ and the membrane, and $R_C^*$ is the interface resistance between the nanowire, deposited Pt-C, and underlying Pt electrode according to

$$R_C^* \approx \frac{4}{\alpha_{1-2} C_1 v_1}.$$  

(4.4)

The transmission coefficient $\alpha_{1-2}$ for heat moving across the interface from Material 1 to Material 2 was calculated according to

$$\alpha_{1-2} = \frac{C_2 v_2}{C_1 v_1 + C_2 v_2}$$

(4.5)

where $C_i$ and $v_i$ are the heat capacity and group velocity of the materials at the two sides of the interface, i.e., the bismuth oxide and the Pt-C contact. The transport properties of the Pt-C contact material were unavailable. Instead the above calculation was performed for limiting cases of either 100% Pt or 100% amorphous C composition with the assumption that the thermal contact resistance of the Pt-C falls between the results for the two constituent materials. The properties of Pt, C, and Bi$_2$O$_3$ at 300 K and 100 K used in this calculation are shown in Table VII while the obtained transmission coefficients and
thermal contact resistances shown in Table VIII. For comparison, the measured total 
thermal conductance (resistance) values for NW3 were 38 nW/K (0.026 K/nW) and 36 
nW/K (0.028 K/nW) at 300 K and 100 K, respectively. Since bismuth oxide is insulating, 
electronic thermal transport across the interface is ignored.

Table VII. Heat capacity (C) and sound velocity (v) of the constituent materials used in 
the thermal contact resistance calculation.

<table>
<thead>
<tr>
<th>Material</th>
<th>300K</th>
<th>100K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (J/g-K)</td>
<td>v x 10^-5 (m/s)</td>
</tr>
<tr>
<td>Bi_2O_3</td>
<td>0.244^a</td>
<td>2.20^b</td>
</tr>
<tr>
<td>Pt</td>
<td>0.133^c</td>
<td>2.68^d</td>
</tr>
<tr>
<td>Amorphous C</td>
<td>0.97^f</td>
<td>11.46^f</td>
</tr>
</tbody>
</table>

^a Polycrystalline data (Barin and Knacke 1973) 
^b (Rabukhin and Belousova 1993) 
^c (Weast 1981) 
^d (Samsonov 1968) 
^e (Moelle, Werner et al. 1998) 
^f (Dillon, Ali et al. 2001) 
^g Extrapolated from data in Barin and Knacke (Barin and Knacke 1973) 
^h Graphite data (Touloukian and Buyco 1970)

Table VIII. Transmission coefficient (α_{12}) and thermal contact resistance (R_c) values 
calculated using the properties in Table VII.

<table>
<thead>
<tr>
<th>Contact</th>
<th>300K</th>
<th>100K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α_{12} R_c x 10^{-5} (K/W)</td>
<td>α_{12} R_c x 10^{-5} (K/W)</td>
</tr>
<tr>
<td>Pt-Bi_2O_3</td>
<td>0.611 2.43</td>
<td>0.557 2.63</td>
</tr>
<tr>
<td>C-Bi_2O_3</td>
<td>0.824 2.10</td>
<td>0.483 2.74</td>
</tr>
</tbody>
</table>

Based on the values listed in Table VIII, the calculated thermal contact resistance 
accounted for less than 2% of the total measured thermal resistance of NW3. Hence, the
observed thermal conductivity suppression could not be attributed to thermal contact resistance alone.

Next, the possibility of a higher concentration of point defects or non-isotope impurity scattering in the nanowire than typically in bulk Bi was investigated as a possible mechanism for thermal conductivity suppression. These two scattering processes were not considered in the original development MHS model (Morelli, Heremans et al. 2002) for which the primary interest was on isotope scattering effects. In spite of the high quality crystal structure observed via TEM for NW3, the nanowire could still contain more impurities and point defects than the bulk Bi crystals upon which the model was developed due to the nanowire synthesis method and conditions. The presence of graphite and residual air molecules in the vacuum-pumped evaporation chamber as well as the high temperatures used to evaporate the source Bi powder make it possible that the resulting nanowire samples contained much higher carbon (C) or oxygen (O) impurities than typical for bulk Bi. For the nanowire phonon thermal conductivity calculated from the MHS model, the effects of point defect and non-isotope impurity scattering was accounted for by including an additional phonon mean free scattering time due to point defects, $\tau_{i,ph}$, from an expression used in the original Callaway model (Callaway 1959). This gives the phonon mean free scattering time due to impurities as $\tau_{i,ph}^{-1}(\omega) = A\omega^4$, where $\omega$ is the phonon frequency and $A$ an adjustable parameter related to the point defect type and concentration. With this scattering mechanism included, the calculated $\kappa_{ph}$ for NW3 with diffuse surfaces becomes smaller than the measured thermal conductivity at 100 K when $A$ is larger than $1.3 \times 10^{-41}$ s$^3$. 

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In order to evaluate the feasibility of this possible explanation, the impurity or defect concentration \( c \) that could result in the obtained \( A \) values was estimated. For simplicity, only the case of substituional impurity doping only was considered. For this situation, phonon scattering from the impurity arises due to the size difference-induced local strain fields and mass difference between the impurity and the Bi atoms for which the parameter \( A \) is given by (Klemens 1955; Callaway 1959)

\[
A \approx c \frac{3V^2}{\pi v_{\text{avg}}^3} \left[ \left( 1 - \frac{M_{\text{imp}} - M}{M} \right)^2 + \left( -3.2 \sqrt{\frac{2}{3}} \frac{R_{\text{imp}} - R}{R} \right)^2 \right]
\]  

(4.6)

where \( V \) is the volume per Bi atom, \( \gamma \) is the Grüneisen parameter, \( v_{\text{avg}} \) is the phonon velocity averaged between the three branches, \( M \) is the average mass of a Bi atom, \( R \) is the atomic radii of a Bi atom, \( M_{\text{imp}} \) is the average mass of the impurity atom, and \( R_{\text{imp}} \) is the atomic radii of the impurity atom. For impurity species such as C, O, or copper (Cu) with small mass and size in comparison to the large and heavy Bi atom, \( A=1.3 \times 10^{-41} \, \text{s}^3 \) corresponds to impurity concentrations in the range of \( 2.8 \times 10^{19} \, \text{cm}^{-3} \) to \( 2.0 \times 10^{20} \, \text{cm}^{-3} \). A much higher concentration is required to give \( A=1.3 \times 10^{-41} \, \text{s}^3 \) if the impurities are mainly heavy atoms such as lead (Pb) where the mass and size differences from Bi are very small. It should be noted that the estimated impurity concentrations obtained from Equation 4.6 should treated as an upper bound to actual levels since no change in elastic constants between the impurity and the Bi host was accounted for (Klemens 1955). In addition, highly effective scattering of phonon by interstitial or vacancy defects would lead to the same \( A \) value at a lower concentrations than found for substitutional impurities alone.
By comparing the calculated $\kappa_{ph,NW}$ curves in Figure 4.10 and the measurement data for NW3, upper and lower bounds can be placed on the nanowire electronic thermal conductivity $\kappa_{E,NW}$. The upper bound on the electronic thermal conductivity $\kappa_{E}$ is set if the phonon contribution is assumed to be negligible such that the thermal transport is entirely electronic. The bulk electronic thermal conductivity $\kappa_{E}$ in Figure 4.9 is about three times higher than the measured total thermal conductivity $\kappa$ of NW3. Thus, thermal transport by charge carriers in NW3 was suppressed by at least a factor of three compared to bulk. The lower bound to $\kappa_{E,NW}$ is set if the electronic contribution is assumed to be negligible and the phonon contribution to the thermal transport dominates such that $\kappa_{NW} = \kappa_{ph,NW}$ at 100 K. This is the situation associated with the curve in Figure 4.10 for diffuse surface scattering and $A=1.3 \times 10^{-41}$ m$^3$. In addition to being a lower bound on the nanowire electronic thermal conductivity, this scenario also represents the upper bound of the nanowire phonon thermal conductivity. Using this curve, the calculated phonon thermal conductivity at 300 K was subtracted from the room temperature measurement of the total nanowire thermal conductivity value to obtain $\kappa_{E,NW} = 1.89$ W/m-K, the minimum room temperature electronic thermal conductivity of the nanowire. This is four times smaller than the bulk electronic thermal conductivity. Using the upper and lower bound conclusions, the above analyses suggests that the electronic thermal conductivity of NW3 is three to four times smaller than found in bulk Bi in the same crystal direction.

The origins of this suppression of the electronic thermal conductivity were investigated as well. If the carrier concentrations and the electron-hole mobility ratio are the same in the nanowire as in the bulk Bi crystals, the three-to-four fold suppression in
the electronic thermal conductivity would be the result of a corresponding three-to-four fold reduction in the electron and hole mobilities. The mobility of electrons and holes within the nanowire according to Matthiessen’s rule are

$$\mu_{c,NW}^{-1} = \mu_e^{-1} + \mu_{e,B}^{-1} + \mu_{e,i}^{-1}$$

(4.7)

and

$$\mu_{h,NW}^{-1} = \mu_h^{-1} + \mu_{h,B}^{-1} + \mu_{h,i}^{-1}$$

(4.8)

where $\mu_{c,NW}$ and $\mu_{h,NW}$ are the electron and hole nanowire mobilities, respectively, and $\mu_e$ and $\mu_h$ are the bulk electron and hole mobilities, respectively. The terms $\mu_{e,i}$ and $\mu_{h,i}$ were used to account for the possibility of higher impurity and defect concentrations in the nanowire than already accounted for in the bulk mobility data of Michenaud and Issi (Michenaud and Issi 1972). The terms $\mu_{e,B}$ and $\mu_{h,B}$ are the electron and hole boundary scattering mobilities given by

$$\mu_{e,B} = \frac{e l_{eB}}{m_e^* v_{eF}}$$

(4.9)

and

$$\mu_{h,B} = \frac{e l_{hB}}{m_h^* v_{hF}}$$

(4.10)

where $m_e^*$ and $m_h^*$ are the electron and hole conduction effective masses, $v_{eF}$ and $v_{hF}$ are the electron and hole Fermi velocities, and $l_{eB}$ and $l_{hB}$ are the adjustable electron and hole boundary scattering mean free paths, respectively. If the necessary three-to-four fold reduction in mobility from bulk values was entirely due to boundary scattering in the nanowire, the boundary scattering mean free paths would lie in the ranges $l_{eB} \sim 135-200$
nm and $l_{hB} \sim 195-295$ nm. These ranges of values are comparable to the nanowire core diameter of 219 nm, the diffuse surface limit of the charge carrier mean free paths.

However, it is unlikely that the entirety of the observed thermal conductivity reduction is due to boundary scattering alone. As mentioned previously, due to the synthesis method it is necessary to also account for a possibly higher impurity scattering rate ($\tau_{i,eh}^{-1}$) of electrons and hole in the nanowire than in bulk Bi because of a likely higher ionized impurity concentration ($N_i$). Using the Brooks-Herring formula (Ziman 1962), the mobilities due to ionized impurities for electrons and holes are given by

$$\mu_{e,i} = \frac{2^{2/3}}{3^{1/2}} \frac{\varepsilon^2}{Z^2 e^3 m_e^{*1/2}} \left( \frac{k_B T}{N_i} \right)^{3/2} \ln \left( \frac{1 + \frac{8m_e^* k_B T}{q^2 h^2}}{\frac{8m_e^* k_B T}{q^2 h^2}} \right)$$

$$\mu_{h,i} = \frac{2^{2/3}}{3^{1/2}} \frac{\varepsilon^2}{Z^2 e^3 m_h^{*1/2}} \left( \frac{k_B T}{N_i} \right)^{3/2} \ln \left( \frac{1 + \frac{8m_h^* k_B T}{q^2 h^2}}{\frac{8m_h^* k_B T}{q^2 h^2}} \right)$$

(4.11) (4.12)

where $\varepsilon$ is the dielectric constant of Bi (taken to be $99.6 \varepsilon_0$ from (Boyle and Brailsford 1960)), $Z$ is the valence difference between the impurity atom and Bi, and $q$ is the screening radius taken to be $\sim 35$ nm from literature (D.H. Brownell and Hygh 1967; Petrashov, Antonov et al. 1991; Sandomirsky, Butenko et al. 2001). These mobilities were then incorporated into the effective carrier mobilities using Equations 4.7 and 4.8.

Besides changes in the charge carrier mobilities, increased impurity concentration also impacts the electronic thermal conductivity through modification of the Fermi level. Changes in the Fermi level affect the partial Seebeck coefficients $S_e$ and $S_h$ as well as the carrier concentrations $n$ and $p$ which in turn affect the magnitude and the relative contributions to the electronic thermal conductivity. To account for this, it was first
assumed that the concentration of ionized impurities $N_i$ was very close to the total impurity concentration $c$ such that $N_i \approx c$. Due to the small band overlap in bulk Bi, the ionization energy of dopants should lie close to the band edges such that this condition is quite likely. For an n-type dopant such as oxygen, the Fermi level $E_F$ in the Bi nanowire model was adjusted according to the impurity concentration

$$E_F = E_{F0} + k_B T \ln \left( \frac{c}{n_0} \right)$$  \hspace{1cm} (4.13)

where $n_0$ is the intrinsic electron carrier concentration and $E_{F0}$ is the Fermi level with no additional impurities present as found from the bulk Bi Seebeck coefficient data. Similarly, for a p-type dopant such as carbon,

$$E_F = E_{F0} - k_B T \ln \left( \frac{c}{p_0} \right)$$  \hspace{1cm} (4.14)

with $p_0$ being the intrinsic hole carrier concentration.

Using the nanowire thermal conductivity described above, the measurement data can be analyzed taking into account both surface scattering and impurity scattering of electrons, holes, and phonons. Following the most likely scenario from the nanowire synthesis process, $\kappa_{E}$, $\kappa_{ph}$, and $\kappa$ were calculated using the same nanowire diameter as NW3 for the case that the impurity doping is fully ionized, substitutional atoms of either oxygen (O) or carbon (C). Phonon scattering from the nanowire surface was assumed diffuse due to the relative size of the observed nanowire surface roughness compared to the dominant phonon wavelength on the order of 1 nm in the measured temperature range. For the charge carriers, the specularity parameter $p_{eh}$ for electrons and holes was
used as an adjustable parameter along with the impurity concentration $c$. These two fitting parameters were adjusted to fit the measured thermal conductivity of NW3.

When diffuse phonon-surface scattering and a given impurity type is assumed, the fitting of the measurement results could be accomplished with uniqueness and within small margins for both $c$ and $p_{eh}$. Because the phonon thermal conductivity dominates at low temperatures, the impurity concentration $c$ is effectively set by matching the data near 100 K. The electronic thermal conductivity, whose importance grows with increasing temperature, is then set by adjusting $p_{eh}$ to match the data at ambient temperatures. The calculation results obtained in this manner are shown in Figure 4.6 for diffuse phonon surface scattering, both C and O impurity species with $N_i = c = 2.8 \times 10^{19}$ cm$^{-3}$, and $p_{eh} = 0.25$. The two most likely impurity types that were considered here (O and C) are similar in size and mass such that the measurement data could be fit with almost the exact same values $c$ and $p_{eh}$ for both species. Other values of $c$ and $p_{eh}$ would be obtained if the dominant impurity atoms were very different in size and mass from C and O. Despite the uncertainty regarding impurity species and the simplicity of the phonon-impurity scattering model, the calculation was able to demonstrate that the observed thermal conductivity reduction $\kappa$ of the single crystal NW3 from bulk values could be explained by combination of carrier surface scattering and impurity concentration on the order of $10^{19}$ cm$^{-3}$.

For the polycrystalline nanowire samples, the boundary scattering mean free paths for phonons and charge carriers can be smaller than the nanowire diameter due to the presence of grain boundaries. Using the same impurity concentration found above from NW3, the measured thermal conductivity values of NW2, NW4, and NW6 were found to
be fit using phonon boundary scattering mean free paths of 15 - 40 nm and charge carrier-boundary scattering mean free paths of 25 - 40 nm. These thermal conductivity calculation results are also shown in Figure 4.6. A comparable phonon mean free path of 11.8 nm was estimated for nanoporous Bi thin films from measurements of the cross-plane thermal conductivities in the range of 0.08-0.8 W/m-K in work by Song et al. (Song, Shen et al. 2004). In addition, the similar thermal conductivity values measured for the polycrystalline nanowire samples with widely varying diameters strongly indicate that grain boundary scattering dominates over surface scattering. These measurement results suggest that the thermal conductivity can be suppressed more effectively by grain boundary scattering than surface scattering, a concept which has recently been used as a means of increasing $ZT$ in nanocomposite bulk thermoelectric materials (Poudel, Hao et al. 2008).

**CONCLUSION**

The thermal conductivities of individual Bi nanowires synthesized from a template-assisted vapor deposition were measured using a suspended microdevice with serpentine resistance thermometers of the same design as simulated in Chapter 3. The obtained results were then analyzed using analytical methods similar to those developed in Chapter 2 and the possible causes of the thermal conductivity suppression from bulk Bi values were identified; namely, increased carrier scattering from point defects, diffuse or nearly diffuse nanowire surfaces, and, in the case of the polycrystalline samples, scattering from grain boundaries. The similar thermal conductivity values measured for polycrystalline nanowires of varying diameter demonstrate the effectiveness of grain boundary scattering in suppressing the thermal conductivity as compared to surface
scattering. However, the effect of grain boundaries on the electrical transport of Bi nanowires would need to be further investigated in order to determine the overall impact on thermoelectric performance as grain boundary scattering of charge carriers would also reduce the electrical conductivity as well. In addition, the nearly diffuse charge carrier scattering obtained from the analytical modeling would have serious effects even in single crystal nanowires on the electrical conductivity due to reduction of the typically long carrier mean free paths found in bulk Bi.
Chapter 5: Thermoelectric Properties of HMS Nanostructures

In this chapter, measurement and analysis of the thermoelectric transport properties of higher manganese silicide (HMS) nanostructures is presented. Suspended microdevices similar to the serpentine heater and line heater designs analyzed in Chapter 3 were used for measurements, while a limited theoretical model similar to that used for CrSi$_2$ nanowires in Chapter 2 was employed to estimate the charge carrier mobility in the nanostructures as compared to bulk. The combined results of the measurements and analysis are then used to comment on the potential of HMS nanostructures for realizing high $ZT$.

INTRODUCTION

Several bulk semiconducting silicides such as CrSi$_2$, Mg$_2$Si, and FeSi$_2$ have been shown previously to be passable high temperature thermoelectric materials with peak $ZT$ values somewhat less than unity between 500 K-1000 K (Rowe 1994; Borisenko 2000). This temperature range of peak $ZT$ makes semiconducting silicides attractive for power generation or energy scavenging applications especially from combustion systems. In addition, these abundant silicon-based materials are known to be mechanically robust, possess exceptional oxidation resistance, and in most cases are more economically viable than other more complex or Ge-based thermoelectric materials.
This work focuses on higher manganese silicide (HMS), a family of compounds with the general stoichiometry $\text{Mn}_n\text{Si}_{2n-m}$ which are typically identified by their more common names MnSi$_{1.75}$ or MnSi$_{1.8}$ (Higgins, Schmitt et al. 2008). Bulk MnSi$_{1.8}$ has been reported with a peak $ZT$ of up to 0.7 at 800 K (Rowe 1994).

In contrast to the metallic material manganese monosilicide MnSi, HMS phases are degenerately p-type semiconductors belonging to a group known as Nowotny chimney ladder phases (Ye and Amelinckx 1986; Rowe 1994; Higgins, Schmitt et al. 2008). These phases are comprised of two mismatched atomic sublattices intertwined to form the atomic unit cell. In the case of HMS, the “chimney” portion of the structure is the tetragonal Mn subcell with a $\beta$-Sn structure, while the almost face centered cubic configuration of Si atoms form the “ladder” of the unit cell (Higgins, Schmitt et al. 2008). As a result of the mismatching Si subcell sizes between phases, numerous HMS phases can have similar lattice constant $a$ with a wide variation in the $c$ lattice constant. Additionally, the sublattice mismatch can lead to $c$ as long as 12 nm. (Higgins, Schmitt et al. 2008). A large lattice constant along the $c$ axis produces a very small first Brillouin zone in the corresponding direction which has important ramifications on phonon transport within the material.

When a material with large $c$ is in the form of a nanostructure, interesting and potentially useful size effects could occur beyond those typically studied for thermoelectric nanostructures. For example, consider the case of an HMS nanowire with the $c$ axis oriented in the radial direction. The largest allowable phonon or electron wavevector in the radial direction would be limited to be close to $\pi/c$, i.e. the size of the first Brillouin zone. In addition, the allowable wavevectors along the same direction
must also be discrete with values of \( \pi/nd \), where \( d \) is the nanowire diameter and \( n \) is an integer. Combining these wavevector requirements, for a nanowire with growth direction perpendicular to the long \( c \) axis and a diameter of tens of nanometers, only a few allowable wavevector states would exist. This would lead to 2D carrier subbands with appreciable separation in the direction corresponding to the \( c \) axis. In contrast, the wavevectors in other crystallographic directions with lattice constant \( a < c \) would likely not experience such quantization due to their larger first Brillouin zone.

Besides being an interesting system for studying transport physics, the confinement of energy transport in HMS nanostructures can potentially lead to enhanced \( ZT \) from the already respectable bulk values. As described in Chapter 1, a typical route to \( ZT \) enhancement in nanostructures pursued by researchers involves reduction in the phonon thermal conductivity from increased phonon-boundary or phonon-interface interactions with decreasing size. Confinement effects on the phonon dispersion relation like those described for HMS above are not expected in typical semiconductor nanowires such as those made of silicon or III-V materials. Thus, the modified phonon transport expected in HMS nanowires represents a novel approach to further reducing the phonon thermal conductivity and improving \( ZT \).

Another advantages of metal silicide nanostructures lie in their expected bulk-like electrical transport properties due to very large carrier effective mass, short carrier wavelength, and small mean free path as found in bulk silicides (Lange, Brehme et al. 1997). The short carrier wavelength makes quantum confinement of charge carriers highly unlikely. In addition, the short intrinsic mean free paths and large effective masses give relatively low bulk mobility values (Kawasumi, Sakata et al. 1981) such that
boundary scattering of charge carriers in a nanostructure is not expected to greatly reduce the charge carrier mobilities from bulk values. This principle has been shown previously for the CrSi$_2$ nanowires in Chapter 2 with large carrier effective mass (Zhou, Szczech et al. 2007) in contrast to the situation observed in the InSb nanowires in Chapter 2 which showed a marked reduction in mobility from the bulk values of $\sim 70,000$ cm$^2$/Vs at 300 K (Seol, Moore et al. 2007; Zhou, Moore et al. 2010). For the CrSi$_2$ nanowires which did not possess a Nowotny chimney ladder crystal structure, strong thermal conductivity reduction was not observed due to the short intrinsic phonon mean free path of the material (Zhou, Szczech et al. 2007). However, the combination of bulk-like electronic transport and uniquely constrained thermal transport could result in significant $ZT$ enhancement in HMS nanostructures.

**METHODS**

HMS nanostructures were synthesized by the Jin group at University of Wisconsin-Madison using a chemical vapor transport (CVT) method. Details of their growth method and sample characterization can be found elsewhere (Higgins, Schmitt et al. 2008). Following the CVT growth, the resulting samples are a mixture of HMS nanowires and nanoribbons anchored at one end to the growth substrate. Pieces of the growth substrate were then placed in a small volume of isopropyl alcohol (IPA) and gently sonicated to release the HMS nanostructures from the substrate surface, creating a fluidic suspension of HMS nanowires and nanoribbons for drop casting onto suspended microdevices for thermoelectric property measurement. In this work, both the serpentine heater design with 200 $\mu$m beams and the liner heater design analyzed in Chapter 3 were used for the transport property measurement. Following successful trapping of an
individual nanostructure sample on a microdevice, beam-assisted deposition of Pt-C contacts were used to improve the electrical and thermal contact resistance between the nanostructure and the patterned Pt electrodes. An example of an HMS sample with Pt-C contacts on a suspended microdevice is shown in Figure 3.7. To minimize the possibility of beam-induced sample damage or Pt-C spreading, electron beam deposition was used on all samples unless otherwise noted. While preferable to ion beam deposition in terms of sample safety, the use of electron beam deposition also led to less reliable electrical contacts. For samples without electrical contact only the two-probe thermal conductivity could be measured. Alternatively, the Seebeck coefficient and the electrical conductivity were also measured using a substrate-based device similar to the one used in the early InSb nanowire work (Seol, Moore et al. 2007) mentioned in Chapter 2. An SEM image of an HMS sample measured using this approach is shown in Figure 5.1.

Figure 5.1: Substrate-based device used for measuring the Seebeck coefficient and electrical conductivity of individual HMS nanostructures. The device-level image in (a) and the detail of the sample region in (b) show the heater line, four electrodes labeled E1 – E4, and two four-probe resistance thermometers labeled T1 and T2.
Due to the lack of a suspended sample region over a through etched hole as in the suspended microdevices, TEM characterization of these samples was not possible. The diameter of the HMS nanowires measured using the substrate-based devices were measured using both SEM and atomic force microscopy (AFM).

Following measurement, the HMS phase, structure, growth direction, and crystal quality were characterized using TEM analysis when possible. For nanowire samples, the transport cross section was determined unambiguously by measuring the HMS core diameter and amorphous surface oxide layer thickness with TEM. For nanoribbon samples, however, only the nanoribbons width and the oxide thickness on the sides of the sample are able to be measured from the limited top-down view of the TEM. It is then not possible to measure the thickness of the HMS core or the thickness of the amorphous oxide layer on top and bottom of the sample with TEM unless the sample is naturally twisted within the suspended region. Instead, the total thickness of the HMS core and oxide was measured using high-angle tilted SEM or AFM of the sample region lying on the device membrane region. For nanoribbons and nanowire samples for which TEM was not obtained, the total dimensions (diameter for nanowires, width and thickness for nanoribbons) including the amorphous oxide layer were measured by SEM images taken prior to measurement. For consistency between samples, the thermal and electrical conductivity as determined from the measured thermal and electrical conductance values were calculated based on the total (oxide included) cross section. For the thermal conductivity calculation, the amorphous oxide layer of unknown composition is also capable of conducting heat albeit with different thermal transport properties than the HMS core. However, the expected composition of the amorphous oxide is expected to be some type of silicon oxide for which the thermal conductivity would be similar to the measured values of the HMS nanostructures (Cahill and Pohl 1987). In this case, the
inclusion of the oxide layer would not significantly affect the overall thermal conductivity result. For the electrical conductivity calculation, however, it should be noted that the amorphous oxide layer should be insulating such that strictly speaking only the cross section of the conducting HMS core region should be used in the calculation of the nanostructure’s electrical conductivity. Thus, the electrical conductivity calculated using the total cross section as described above should be viewed as a lower bound of the actual HMS sample electrical conductivity.

RESULTS

A summary of the measured samples is given in Table IX including information obtained from TEM characterization performed by Jeremy Higgins at UW-Madison. As mentioned previously, some samples were broken during preparation for TEM following measurement. All samples studied with TEM were single crystal within the beam spot and no grain boundaries were observed during imaging. A representative TEM image and diffraction pattern from NR 1 are shown in Figure 5.2.

Figure 5.2: TEM analysis of NR 1. (a) High resolution TEM (HRTEM) image. (b) Fast Fourier transform (FFT) image. (c) Selected-area electron diffraction (SAED) image.
Table IX. Summary of the measured HMS samples. Nanoribbon samples are denoted “NR” while nanowire samples are labeled with “NW”. The measured properties indicate two-probe (2p) and four-probe (4p) measurement type for the Seebeck coefficient ($S$), electrical conductivity ($\sigma$), and thermal conductivity ($\kappa$). The device used for each sample are indicated as serpentine heater microdevice (SHMD), line heater microdevice (LHMD), or substrate device (SD). The dimensions refer to thickness and width for nanoribbons and diameter for nanowires.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dimensions (nm)</th>
<th>Crystal Information</th>
<th>Properties</th>
<th>Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR 1</td>
<td>24 x 153</td>
<td>Perp. to the {121}, 63° off c axis, Mn$<em>{36}$Si$</em>{68}$ with c~17nm</td>
<td>4p (S),4p (\sigma),4p (\kappa)</td>
<td>LHMD</td>
</tr>
<tr>
<td>NR 2</td>
<td>53 x 261</td>
<td>Perp. to {121}</td>
<td>2p (\kappa)</td>
<td>SHMD</td>
</tr>
<tr>
<td>NR 3</td>
<td>46 x 79</td>
<td>Perp. To {332}</td>
<td>2p (S),2p (\sigma),2p (\kappa)</td>
<td>LHMD</td>
</tr>
<tr>
<td>NR 4</td>
<td>25 x 153</td>
<td>-</td>
<td>2p (\kappa)</td>
<td>SHMD</td>
</tr>
<tr>
<td>NW 1</td>
<td>67</td>
<td>Perp. to {112}</td>
<td>2p (\kappa)</td>
<td>SHMD</td>
</tr>
<tr>
<td>NW 2</td>
<td>51</td>
<td>-</td>
<td>2p (\kappa)</td>
<td>SHMD</td>
</tr>
<tr>
<td>NW 3</td>
<td>62</td>
<td>-</td>
<td>2p (S),4p (\sigma)</td>
<td>SD</td>
</tr>
<tr>
<td>NW 4</td>
<td>63</td>
<td>-</td>
<td>2p (S),4p (\sigma)</td>
<td>SD</td>
</tr>
</tbody>
</table>

The measured thermal conductance values for the HMS nanostructure samples are shown in Figure 5.3 along with the background thermal conductance measured using a blank device as described in Chapter 4. The resulting thermal conductivities obtained using the total cross section and subtracting the corresponding microdevice’s background thermal conductance values are shown in Figure 5.4. The thermal conductivity of the HMS nanostructures is consistently below all bulk values, with the thermal conductivity of NR 1 being roughly half of the bulk thermal conductivity expected along the same crystal direction. In comparison, the minimum thermal conductivity for HMS as estimated to be 0.73 W/m-K at 300 K using the model by Cahill et al. (Cahill, Watson et al. 1992).
Figure 5.3: Measured thermal conductance of values of HMS nanostructures and blank microdevices.
Figure 5.4: Thermal conductivity of HMS nanostructures. Also shown are values for various forms of bulk HMS including single crystal data in the c direction and a-b plane (Rowe 1994). The solid red line is the expected single crystal bulk properties along the same crystal orientation as NR 1 as calculated from the Thompson-Voigt relation (Gallo, Chandrasekhar et al. 1963). The symbols for the HMS nanostructures are the same as in the legend of Figure 5.3.

For the four-probe sample NR 1, the four-probe thermoelectric measurement method (Mavrokefalos, Pettes et al. 2007) was used to measure the transport properties as well as obtain the thermal contact resistance between the sample and the membranes.
The thermal contact resistance for this nanoribbon sample was found to be \( \sim 8\% \) of the total measured thermal resistance, indicating that the thermal conductance measured for other HMS samples using a two-probe thermal measurement (Shi, Li et al. 2003; Yu, Saha et al. 2006) were likely to be dominated by the sample thermal conductance rather than contact resistance effects.

The measured Seebeck coefficient data for the HMS nanostructures is shown below in Figure 5.5 along with bulk HMS data. The positive values indicate that the samples were p-type with Seebeck magnitudes comparable or somewhat smaller than the range of bulk values. As discussed in Chapter 2 for the Bi\(_2\)Te\(_3\) nanowires, a reduced Seebeck magnitude could be the result of either a near-transition, two-carrier system or a highly doped sample with Fermi level well within the respective dominant single-carrier band. However, considering that HMS is naturally degenerately p-type within the measured temperature range (Kawasumi, Sakata et al. 1981) and has an electron-to-hole mobility ratio of 0.02 (Nishida 1972), the two-carrier scenario is highly unlikely. The most likely explanation is unintentional impurity doping introduced either during sample growth or sample preparation. Alternatively, in bulk HMS boules natural precipitation forms striations of metallic MnSi within the samples. The bulk data presented in the HMS plots of the thermoelectric properties has been compensated to remove the influence of these MnSi regions and represent the true transport properties of HMS alone. Though no such MnSi striations were observed during TEM analysis of the samples, the presence of metallic MnSi in Si-deficient regions of the samples might also act reduce the Seebeck coefficient to slightly below the bulk values.
Figure 5.5: Seebeck coefficient of HMS nanostructures. Also shown are values for various forms of bulk HMS including single crystal data in the c direction and a-b plane (Rowe 1994). The solid red line is the expected single crystal bulk properties along the same crystal orientation as NR 1 as calculated from the Thompson-Voigt relation (Gallo, Chandrasekhar et al. 1963). The symbols for the HMS nanostructures are the same as in the legend of Figure 5.3.

The four-probe electrical conductivity obtained using the total cross section for the HMS nanostructures is shown in Figure 5.6 along with bulk HMS data. Though two-probe electrical conductivity data was obtained for several samples, this data has been excluded due to the presence of contact resistance and to preserve clarity in regards to the true thermoelectric potential. Even using the total cross section including the insulating amorphous surface oxide the electrical conductivity is still comparable to the lower values of bulk HMS. Since the Seebeck coefficient data suggests only light or moderate
impurity doping, the comparable electrical conductivity results suggest that the HMS nanostructures retain bulk-like electrical transport and do not suffer the drastic mobility reduction observed for other nanostructures. This question will be explored in more detail in the following section. The $ZT$ obtained for the four-probe sample NR 1 is shown in Figure 5.7 is shown along with bulk HMS data.

![Graph of electrical conductivity](image)

**Figure 5.6:** Electrical conductivity of HMS nanostructures. Also shown are values for various forms of bulk HMS including single crystal data in the $c$ direction and $a$-$b$ plane (Rowe 1994). The solid red line is the expected single crystal bulk properties along the same crystal orientation as NR 1 as calculated from the Thompson-Voigt relation (Gallo, Chandrasekhar et al. 1963). The symbols for the HMS nanostructures are the same as in the legend of Figure 5.3.
Figure 5.7: $ZT$ of HMS nanostructure samples NR 1 as compared to values for various forms of bulk HMS including single crystal data in the $c$ direction and $a$-$b$ plane (Rowe 1994). The solid red line is the expected single crystal bulk properties along the same crystal orientation as NR 1 as calculated from the Thompson-Voigt relation (Gallo, Chandrasekhar et al. 1963). The symbols for NR 1 are the same as in the legend of Figure 5.3.

**ANALYSIS**

The available means of analytically modeling the measurement results are more limited for this material system than for others already analyzed in this work. However, several important points can still be made regarding energy transport in HMS nanostructures. First, the origin of the observed thermal conductivity reduction could occur due to either classical boundary scattering or the quantum effects discussed in the introduction to this chapter. The phonon mean free path is generally smaller in metal
silicides than in other thermoelectric materials. High energy, short wavelength phonons have short mean free paths due to strong phonon-phonon scattering in bulk such that the influence of nanostructure boundaries on these phonons may not be appreciable. However, long wavelength phonons can have much longer mean free paths such that their thermal conductivity contribution should still be reduced from bulk values when the size of the nanostructure is on the order of tens of nanometers especially below room temperature.

The thermal conductivity plateau that is seen in bulk HMS has been attributed to a substantial contribution of optical phonons to both the phonon scattering rates and thermal transport (Rowe 1994). Optical phonons are known for having much lower group velocity than their acoustic branch counterparts and, as a result, a shorter mean free path for similar scattering rates. It is then possible that the nanostructure geometry limits the long wavelength acoustic phonon mean free path while retaining bulk-like transport for optical phonons. Thus, the acoustic phonon contribution would be reduced and the measured thermal conductivity values are even more dominated by optical phonons than in bulk. However, there is temperature dependence to this picture as well. As temperature decreases the acoustic phonon mean free path would be increasingly constrained by the nanostructure while the occupation probability of the high energy optical modes is reduced. Thus at low temperatures it is difficult to say qualitatively which effect more strongly reduces the thermal conductivity. Similarly, as temperature increases the acoustic phonon mean free path becomes shorter until it becomes smaller than the nanostructure dimensions due to phonon-phonon scattering. At the same time, the occupation of high energy optical phonons increases as well which could increase the thermal conductivity. Ideally, this acoustic and optical phonon dominance picture could be further investigated using analytical thermal conductivity models similar to those used
in the prior nanowire works (Mavrokefalos, Moore et al. 2009; Moore, Pettes et al. 2009; Zhou, Moore et al. 2010). However, the model developed by Morelli et al. (Morelli, Heremans et al. 2002) used in those works was for acoustic phonons only and relied on knowledge of the phonon dispersion relation which has not been studied for HMS.

![Figure 5.8: Extracted hole concentration for HMS nanostructure samples as compared to bulk single crystal data (Kawasumi, Sakata et al. 1981).](image)

The Fermi level and carrier concentration for the HMS samples with Seebeck coefficient data were obtained using the same 3D Seebeck model used in the CrSi$_2$ nanowire work in Chapter 2 using $m_h^* = 12m_0$ and $r_h = -0.5$ as done for bulk HMS in Nishida (Nishida 1972) and Kawasumi et al. (Kawasumi, Sakata et al. 1981). It is also possible to obtain hole mobility values for samples with four-probe electrical conductivity using $\sigma = pe\mu$. However, as noted previously these values would represent the lower bound of the actual mobility due to the use of the total cross section rather than
the HMS core cross section. The results, when plotted and compared to bulk values, would then be misleading low and are thus not presented in this work. The results for the hole concentrations as compared to bulk HMS data are shown in Figure 5.8. As initially suggested by the Seebeck and electrical conductivity measurement data, the obtained carrier concentrations for the HMS nanostructures were comparable to or slightly higher than bulk HMS levels.

CONCLUSION

Thermoelectric transport measurements were performed on HMS nanowires and nanoribbons using both suspended and substrate-supported microdevices. TEM analysis of multiple samples showed high crystal quality with growth direction between the c and a-b crystal directions. Measurement results showed a consistently 2 to 4 times lower thermal conductivity for the HMS nanostuctures as compared to bulk, although the exact mechanism by which this occurs is not fully understood. Seebeck coefficient values were comparable to or smaller than bulk HMS values, suggesting that the samples were unintentionally doped at some point. Accurate determination of the oxide layer thickness for nanoribbons morphologies necessitated the use of the total nanostructure cross section be used in the transport coefficient calculations, thus making the as-obtained electrical conductivity serve as a lower bound to the actual values of the HMS core. The resulting conservative four-probe ZT values for an HMS nanoribbon were comparable to those expected for bulk HMS along the same crystal direction. Analytical modeling showed comparable or higher carrier concentration than bulk levels. If the nanoribbons core dimensions were able to be accurately determined the electrical conductivity and ZT would be increased from their plotted values. Together, the measurement results and analysis show that the concept of achieving thermal conductivity reduction coupled with
bulk-like electrical transport as a means of improving $ZT$ in HMS nanostructures is promising and worthy of future study. Further work remains to be done to measure the four-probe properties of additional samples in addition to improving methods for making reliable electrical contact to samples and determining the HMS core dimensions of nanoribbons samples. These may require changes to the current suspended microdevice designs which can then be used to improve measurements of other nanostructure systems.
Chapter 6: Conclusion

This work presented the development and application of analytical, numerical, and experimental methods for the study of thermal and electrical transport in nanoscale systems. Using established solutions to the Boltzmann transport equation (BTE) using the relaxation time approximation (RTA), the measurement results for several thermoelectric nanowire systems were analyzed and valuable information regarding their performance and future potential for \( ZT \) enhancement were obtained. A need for better impurity control during growth was determined for both the InSb and Bi\(_2\)Te\(_3\) nanowire systems from the BTE-based extraction of Fermi level and calculated carrier concentration. More limiting, however, to the future of these nanowire systems for thermoelectric applications was the reduced charge carrier mobility found for these systems found from the BTE models. Though mobility reduction due to surface states or defects can be solved in principle, the mobility reduction associated with strong carrier-boundary scattering would still be present. This indicates that even with optimized doping levels, the electrical conductivity in these systems could be reduced to a much greater extent than the thermal conductivity, resulting in inferior \( ZT \) to bulk. For CrSi\(_2\) nanowires, however, using the BTE modeling approach bulk-like electrical transport was observed due to the large carrier effective mass and intrinsically short charge carrier mean free paths smaller than the nanowire diameters. The obtained hole concentrations and mobility were shown to be comparable to bulk values, further supporting this new
approach of using low mobility metal silicide materials to realizing $ZT$ enhancement in nanostructures.

The RTA-based BTE methods used in modeling nanoscale electrical transport were shown to be both powerful and flexible, being used for both single-band and two-band systems in simple and complex analyses. However, the RTA does not work in every situation as illustrated in the modeling of phonon transport in SiO$_2$-supported single layer graphene. The RTA expression for the umlapp phonon-phonon scattering in graphene gives a negligible contribution to the thermal conductivity from the ZA phonon branch in suspended and supported graphene, while a separate full quantum mechanical BTE solution which does not rely on the RTA predicts a dominant ZA contribution in suspended graphene. The measurement results for this situation were poorly matched by the RTA-based BTE phonon model, while the quantum mechanical model showed excellent agreement when strong substrate scattering of the ZA phonon mode was considered. Besides the important measurement result alone, the associated analysis also improved the understanding of heat conduction physics in single layer graphene as well as the limitations of the RTA-based scattering model to accurately describe phonon-phonon scattering in single layer graphene. Thus, RTA-based methods are convenient, powerful, and useful in many situations, but their validity in modeling nanoscale energy transport must be determined on a case-by-case basis and may not work for all systems. As an alternative to analytical solution methods, the BTE may also be solved statistically through numerical Monte Carlo simulation. An example of this approach was shown through the use of Monte Carlo methods to investigate phonon transport in Si nanowires with sawtooth surface facets. The results showed that thermal conductivity values below
the diffuse surface limit could be obtained in the presence of scattering-promoting surface roughness. The Monte Carlo simulation of phonon transport in nanostructure is still relatively new compared to other modeling techniques, but the methods, capabilities, and popularity of this approach are increasing and look to progress beyond the basic thin film and nanowire geometries commonly studied to more complex and device-oriented domains in the near future.

The experimental study of thermal and thermoelectric energy transport in nanostructures typically involves either the use of microfabricated devices or interaction by a non-contact optical method. Examples of both approaches were analyzed in this work in order to determine the accuracy and applicability of the respective measurement designs. Through traditional analytical heat transfer analysis of the Raman measurement of suspended and supported CVD single layer graphene, the thermal interface conductance, thermal contact resistance, and thermal conductivity of both the supported and suspended graphene regions were able to be determined from the measurements. In addition, the impact of the Gaussian-like beam shape and finite beam size were able to be accounted for and their relative impact on the resulting thermal resistance understood. This detailed analysis provided a more complete understanding of this measurement method and the important parameters influencing its accuracy and capabilities, thereby helping to identify areas which can still be improved upon in future work such as minimizing air losses, improved temperature calibration, and larger sample sizes.

Finite element simulations of several suspended microdevice designs were also performed using ANSYS in order to determine both the validity of their associated conduction analyses and their overall thermal behavior. Using samples of known thermal
conductance, the discrepancy between the known sample thermal conductance and that obtained from the simulated measurement and associated conduction analysis was found to be small compared to the typical random measurement uncertainty for the suspended sample (serpentine and line heater) designs provided that radiation losses were negligible. However, it was found that radiation losses could impact the measurement results indirectly prior to the actual measurement cycle through errors in the resistance thermometer calibration procedure. As a result of this finding, a radiation shield adjacent to the sample space attached to the same cold finger as the device package was incorporated into the cryostat setup. For device designs in which the sample is supported by a “bridge” whose thermal conductance is later removed by subtraction, the discrepancies between the known sample thermal conductance and the simulated measurement and associated conduction analyses were generally larger than those found for the suspended sample designs. It was found that for these bridge device designs having a uniform sample cross section, i.e. having the supported sample region the same width of the bridge, was preferable from a conduction analysis point of view to having a localized sample region.

The experimental and analytical methods outlined in the beginning of this dissertation were employed in the measurement and analysis of the thermal conductivities of individual bismuth nanowires synthesized from a template-assisted vapor deposition method. The results showed strong thermal conductivity suppression from bulk values, especially in the polycrystalline samples. From analytical modeling, this suppression was explained in terms of increased carrier scattering from point defects, diffuse or nearly diffuse nanowire surfaces, and, in the case of the polycrystalline samples, scattering from
grain boundaries. The similar thermal conductivity values measured for polycrystalline nanowires of varying diameter demonstrate the effectiveness of grain boundary scattering in suppressing the thermal conductivity as compared to surface scattering. However, the effect of grain boundaries on the electrical transport of Bi nanowires would need to be further investigated in order determine the overall impact on thermoelectric performance as grain boundary scattering of charge carriers would also reduce the electrical conductivity as well. In addition, the nearly diffuse charge carrier scattering obtained from the analytical modeling would have serious effects even in single crystal nanowires on the electrical conductivity due to reduction of the typically long carrier mean free paths found in bulk Bi. As with several nanowire systems of interest, the ability to make reliable electrical contact to suspended nanowire samples while maintaining sample integrity remains a key technological and experimental challenge.

Using similar experimental methods as using for the bismuth nanowire work, the thermoelectric transport properties of higher manganese silicide (HMS) nanowires and nanoribbons were measured using suspended and substrate-based microdevices. This material system could exhibit the bulk-like electrical transport observed in CrSi$_2$ nanowires but with the potential for significant thermal conductivity reduction in nanostructure form. Measurement results showed a consistently lower thermal conductivity for the HMS nanostructures as compared to bulk, although the exact mechanism by which this occurs could not be identified due to analytical modeling limitations. The measured Seebeck coefficient values were comparable to or smaller than bulk HMS values likely from unintentionally doping either during growth or sample preparation. Accurate determination of the oxide layer thickness for the nanoribbon and
SEM-only samples necessitated the use of the total nanostructure cross section be used in the transport coefficient calculations. This fact limits the electrical conductivity to act as a lower bound to the actual values of the HMS core, a fact that makes comparison to bulk values problematic. Data analysis using an RTA-based BTE model similar to that used previously for CrSi$_2$ nanowires showed comparable or higher carrier concentration than bulk levels. The resulting conservative four-probe $ZT$ values for an HMS nanoribbon were comparable to those expected for bulk HMS along the same crystal direction, with the electrical conductivity and $ZT$ expected to increase from their plotted values if the nanoribbons core dimensions were able to be accurately determined. Together, the measurement results and analysis show that the concept of achieving thermal conductivity reduction coupled with bulk-like electrical transport as a means of improving $ZT$ in HMS nanostructures is promising and worthy of future study. Further work remains to be done to measure the four-probe properties of additional samples in addition to improving methods for making reliable electrical contact to samples and determining the HMS core dimensions of nanoribbons samples. These may require changes to the current suspended microdevice designs which can then be used to improve measurements of other nanostructure systems. In addition, improved control over the sample doping and crystal orientation in order to maximize the electrical properties and thermal conductivity suppression could lead to higher $ZT$.

Though performed for specific material systems, nanostructure types, and measurement designs, this work can also serve as a more general example of several current analytical, numerical, and experimental methods used in the study of nanoscale energy transport. It also demonstrates that a combination of experimental and theoretical
approaches is often required to fully understand the sometimes complex transport processes occurring within a nanostructure or device. As small scale systems continue to develop and become increasingly important in engineering and science applications, the ability to use and understand multiple analysis and experimental methods will be come increasingly important as well, further facilitating the need for researchers in this area to collaborate with others and diversify their own research skills.


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