Chapter 1

OVERVIEW

1.1 Nanoscale energy transport

The ability to tailor the fundamental physical properties of materials and devices exactly at the scale where they occur requires atomically precise control of matter. Modern technologies provide new approaches to use structure at the nanoscale as a tunable physical variable, which allows us to greatly expand the range of performance of existing materials and devices. One of the prominent topics in nanoscience is the ability to manipulate heat transport at the scales of energy carriers in solids. Precise control of heat could lead to efficient heat dissipation in high power and nanoscale electronic devices, the proposed use of intensely heated nanoparticles in medical therapies, and waste heat harvesting using thermoelectric devices in automobiles and airplanes.

Over the past decades, extensive research in nanoscale energy transport has led to remarkable advances such as the demonstration of thermoelectric materials with exceptionally high efficiencies. Recently, nanocrystalline materials, which are polycrystalline materials with nanoscale grain sizes, have been demonstrated as efficient thermoelectrics. Many of these materials show great promise for scalable manufacturing. In particular, the nanostructuring approach has been successful for silicon and silicon-germanium alloys created by ball-milling and hot pressing. SiGe has long been used for space power generation(*1*, *2*) and the thermoelectric properties of SiGe nanocomposites with improved properties over those of the bulk were recently reported.(*2–5*) Substantial improvements in nanostructured bulk silicon, which does not require expensive and rare germanium, were also reported.(*6*)

Research in engineering interfaces between two solids enables new functionalities that are not possible in homogeneous materials. For instance, electronic transport across metal-semiconductor and pn-junctions forms the basis for modern microelectronics, photovoltaics, and light-emitting diodes (LEDs). Interfaces play a key role in heat conduction by phonons as well: engineered interfaces in solids have led to dramatic increases in the efficiency of thermoelectric materials.

Anisotropic materials, which can possess extreme values of thermal conductivity that are difficult to achieve in isotropic materials, has been used to control heat flow in different crystal orientations.(*7*) For example, the extremely high thermal conductivity in the basal plane and low thermal conductivity in the cross plane makes graphite an attractive candidate for heat spreading applications in high-power transistors.(*8*)These are just a few examples of utilizing and engineering materials to gain the desired thermal properties in solids.

To ultimately achieve precise control of heat in solids, the knowledge of heat carriers is crucial. There are two major heat carriers in solids: electrons and phonons. Electrons carry charges as well as heat. In fact, in heavily-doped semiconductors, electrons can contribute up to half of the total thermal conductivity. Phonons are the quantized lattice vibrations in a crystal, which are the domaint heat carriers in dielectrics and semiconductors. While electronic properties in solids, *i.e.* electrical resistivity, optical absorption, and interfacial transmission processes, have been well understood, our knowledge of phonons lags far behind that of electrons.

For instance, the improved efficiency in nanocryatlline thermoelectric materials is achieved by significantly reducing the phonon thermal conductivity through strong phonon grain boundary scattering.(*3*, *4*, *6*, *9–12*) The physics of thermal conductivity is commonly interpreted using kinetic theory

$$k = \frac{1}{3}\sum_{pol}\int C_\omega v_\omega \Lambda_\omega d\omega, \tag{1.1}$$

where C_ω is the mode specific heat, v_ω is the group velocity, ω is the frequency, Λ_ω is the effective mean free path (MFP), and the sum runs over all phonon polarizations. Λ_ω includes all those scattering mechanisms present in a bulk sample, Λ_{bulk}, as well as additional scattering due to grain boundaries, Λ_{bdy}, which are combined using Matthiessen's rule: $\Lambda_\omega^{-1} = \Lambda_{bulk}^{-1} + \Lambda_{bdy}^{-1}$. The greatest challenges to engineer thermal conductivity are in measuring and calculating both Λ_{bulk} and Λ_{bdy}.

The knowledge of bulk mean free paths of solids is crucial to designing nanostructures that could provide optimal thermal properties.(*13*, *14*) Surprisingly, we do not know the MFPs in most solids. First-principle calculations based on density functional theory have enabled the direct computation of MFPs in materials with simple crystal structures. However, they have never been directly measured in experiments. Traditionally, semi-empirical expressions have been the only means to estimate MFPs.(*15*) Various experimental techniques to measure phonon MFPs exists such as photoacoustic wave propagation,(*16*) inelastic neutron scattering,(*17*) heat pulse techniques(*18*, *19*) but they have some limitation such as a restriction on the sample type, accessible phonon frequency range, or applicable temperatures. Recently, Minnich proposed a method(*20*) to accurately reconstruct the MFP distribution over a wide range of length scales and materials from the observation of quasiballistic thermal transport, which occurs if a temperature gradient exists over a length scales comparable to phonon MFPs.(*21*, *22*) The proposed method is suitable of a series of ultrafast optical techniques(*20*, *23–25*) where quasiballistic phonon transport can be observed. However, interpreting measurements using this reconstruction method requires the knowledge of heat conduction beyond the diffusion transport, which is a challenge itself. Thus, measuring phonon MFPs remains a tough task.

Another challenge in engineering thermal conductivity using nanostructures is to predict Λ_{bdy} for the complex interfaces, *i.e.* grain boundaries. Our knowledge

of boundary scattering process is still based on simple models that were developed over 50 years ago and have never been experimentally verified. Numerous works over several decades have investigated the microscopic processes of phonon transport at solid-solid interfaces by observing the temperature dependence of the thermal conductivity or interface conductance(*26–30*) or by correlating changes in bonding strength and interface conductance.(*31*, *32*) However, these experimental approaches provide limited information about the microscopic information about thermal phonons because the observed quantities are averaged over all phonons and thus obscure the microscopic processes of interfacial thermal phonon transport at solid-solid interfaces.

The third challenge is to model heat conduction at length scales comparable to phonon MFPs, which has been of considerable interest recently(*33*) due to its applications in many technologies such as thermoelectrics(*10*, *12*) and electronic devices(*34*) as well as its potential to infer phonon MFP spectra in solids. At these small scales, classic continuum transport theories such as Fourier's law are not valid due to the absence of scattering and therefore a local temperature.(*35*) In this nondiffusive regime, phonon transport is nonlocal and is described by the phonon frequency-dependent Boltzmann transport equation (BTE).(*21*) The BTE is an integrodifferential equation of time, space, and phase space.(*36–39*) It is extremely challenging to solve due to its high dimensionality. Extensive efforts have been done to study phonon transport using BTE.(*40–43*) However, most of the previous approaches depended on simplifications to make the problem tractable, which in practice are not physical. Rigorous methods to model nanoscale heat conduction using the BTE with no or minimal simplifications in various geometries are key components of successfully controlling heat in solids.

1.2 Outline of this thesis

A better understanding of any one of these topics could lead to substantial contribution to our fundamental knowledge of energy carriers. The purpose of this thesis is to give insights into some of these questions. This work focuses on understanding energy transport by phonons at the nanoscale using theory, computational methods and ultrafast experimental techniques.

Chapter 2 studies the impact of frequency-dependent grain boundary scattering in nanocrystalline silicon and silicon-germanium alloys in a realistic 3D geometry using frequency-dependent variance reduced Monte Carlo simulations. We are able to explain the thermal conductivity measurements in nanocrystalline Si by Wang *et. al.* while the commonly used gray model, assuming phonon-grain boundary scattering rate is a constant for all phonon modes, predicts the wrong trend of thermal conductivity at low temperatures. We find that the grain boundary may not be as effective as predicted by the gray model in scattering certain phonons. We also identify the portion of the phonon spectrum that is responsible for carrying heat across the grain boundaries, therefore helping guide the design of more efficient TEs.

While this computational study provides important insights, one issue still remains. Even though the proposed frequency-dependent model reproduces the experimental measurements, the fitting itself is not unique. Since thermal conductivity is a macroscopic property that is integrated over the thermal spectrum, there exists multiple choices of this underlying distribution that result in the same thermal conductivity. Moreover, we do not know the spectral properties of thermal phonons in most of the materials. The second portion of the thesis focuses on determining how to more directly measure properties of the heat carriers like the phonon MFP distribution in bulk materials and phonon transmission coefficients at a solid-solid interface.

In Chapter 3, we present analytical solutions to the phonon Boltzmann transport equation, the governing equation when heat transport occurs at length scales comparable to phonon MFPs. We first derive an analytical Green's function for the frequency-dependent, multidimensional Boltzmann equation under the relaxation-time approximate. Then, we present a semi-analytical series expansion method to solve the transient, frequency-dependent BTE in a thin film geometry. The new solutions are valid from diffusive to ballistic transport regimes and rigorously includes frequency dependence of phonon properties and enables simple closed-form solutions for a number of multidimensional problems for which the only prior solution methods have been computationally expensive numerical methods. Most importantly, the analytical solutions allow us to inspect nanoscale heat conduction just by looking at the expression of the equation, which is not directly accessible from pure numerical approaches.

The rest of the thesis focuses on applying the derived analytical solutions to extract the spectral properties of thermal phonons in bulk materials and at interfaces. Chapter 4 analyzes heat conduction in transient grating (TG) spectroscopy and demonstrates that the new analytical Green's function enables a more accurate measurement of MFP spectra, therefore leading to an improved understanding of heat conduction in solids.

In Chapter 5, we report the first measurements of thermal phonon transmission coefficients at a metal-semiconductor interface using ab-initio phonon transport modeling based on the BTE solutions in Chapter 3 and a thermal characterization technique, time-domain thermoreflectance. With our approach, we are able to directly link the atomic structure of an interface to the spectral content of the heat crossing it for the first time. Our work realizes the long-standing goal of directly measuring thermal phonon transmission coefficients and demonstrates a general route to study microscopic processes governing interfacial heat conduction.

Finally, chapter 6 examines possibilities for future work and concludes the thesis.