Chapter 6

CONCLUSIONS AND OUTLOOK

6.1 Summary

Precise control of thermal phonons, which are the primary heat carriers in solids, is a fascinating and rapidly growing field which could make substantial contributions to greatly expand the range of performance of existing materials and devices as well as innovate new materials and device designs. Interfaces play an essential role in phonon-mediated heat conduction in solids. The ability to manipulate thermal phonons using interfaces could impact applications ranging from thermoelectric waste heat recovery to heat dissipation in electronics. Despite the importance of interfaces and decades of work, interfacial thermal phonon transport remains one of the most poorly understood transport processes. This thesis has explored the physics of interfacial heat transport by phonons, and helped identify how we are able to use atomic structures to control phonon transport in solids. Using a combination of modeling and experiment we are able to better understand phonon transport across interfaces, and we introduce a new approach by which the microscopic properties of thermal phonons can be extracted from thermal measurements.

Chapter 2 has studied the impact of frequency-dependent grain boundary scattering in nanocrystalline silicon and silicon germanium alloys using a novel frequency-dependent variance-reduced Monte Carlo technique. This method allows us to simulate the thermal phonon transport in a realistic 3D geometry of a complex nanograin structure. We find that the grain boundary may not be as effective as predicted by the commonly used gray model in scattering certain phonons, with a substantial amount of heat being carried by low frequency phonons with mean free paths (MFPs) longer than the grain size. Significant potential to improve the

efficiency of nanocrystalline silicon and silicon germanium exists if these phonons can be scattered. Our work provides important insight into how to further increase the thermoelectric performance of nanostructured silicon and silicon-germanium alloys.

The rest of the thesis focuses on how to measure microscopic properties of thermal phonons directly from experimental measurements. In Chapter 3, we have presented two new analytical methods to solve the frequency-dependent, multidimensional Boltzmann transport equation (BTE) under relaxation time approximation that enables simple, closed-form solutions to complex problems that have been tractable previously only using computational expensive simulations. Our new solutions are valid from diffusive to ballistic transport regimes, rigorously including frequency-dependence of phonon properties, and can be applied to complex geometries.

Chapter 4 has applied the analytical methods to study the heat conduction in transient grating (TG) spectroscopy, which has been of intense interest recently because of the possibility of measure MFP spectra using observations of quasiballistic heat conduction. The derived analytical solution provides a more rigorous mathematical formulation to interpret the TG measurement and therefore enables MFP spectra to be measured more accurately.

In Chapter 5, we have reported the first measurement of the transmission coefficients for thermal phonons at a metal-semiconductor interface. Our approach exploits the advances in ab-initio thermal phonon transport modeling we present in Chapter 3 to directly extract the coefficients from the data of an optical thermal experiment for the first time. 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 measurements reveal that phonons with wavelength shorter than the in-

terface roughness are more likely to be reflected by the interface than phonons with wavelength longer than the interface roughness, and as the interface gets rougher, a larger fraction of the phonon spectrum is affected by the interface. In contrast to prior approaches that measure only interface conductance, here we are able to precisely and unambiguously identify which phonons are more likely to be reflected due to atomic-scale changes in the interface structure for the first time. Our work also demonstrates a general approach by which the microscopic properties of thermal phonons can be extracted from thermal measurements, and thus sets the stage for additional seminal measurements.

6.2 Future work

One important conclusion of this thesis is that the combination of ab-initio transport modeling and ultrafast optical techniques could yield tremendous microscopic information about thermal phonons that is not previously accessible only through ultrafast experiments. In a sense, then, the work presented here is only the beginning because it demonstrates a general route by which the microscopic processes of thermal phonon transport can be studied from thermal measurements. With this approach, many other transport processes such as phonon scattering by defects and electron-phonon coupling in semiconductors can be explored.

The future work consists of measuring transmission coefficients for increasingly complex materials. The simplest next step would be to perform similar transmission coefficient measurements at other metal-silicon interfaces for different types of interfaces, *i.e.* atomically smooth or textured interfaces. Then, the method can be extended to study more complicated interface geometries, *i.e.* grain boundaries or superlattices.

Half-Heusler compounds have been attractive thermoelectric materials because they are usually environmentally friendly, mechanically, and thermally robust. However,

their high thermal conductivity has impeded the progress of making them commercially viable. Nanostructured Half-Heusler thermoelectrics has been demonstrated with an improved efficiency. This improvement again is attributed to a reduction in thermal conductivity by grain boundary scattering of phonons as nanocrystalline silicon and silicon-germanium discussed in Chapter 1. However, the microscopic properties of Half-Heusler such as phonon MFPs is still unclear. A systematic study on the microscopic transport processes occurring in nanostructured Half-Heuslers is necessary to further improve their efficiency as thermoelectrics. For future work, one can use the method described in Chapter 4 to measure the MFP spectra in both bulk and nanocrystalline Half-Heusler compounds. By comparing the two spectra, one can get a microscopic quantitative picture of how specific phonons are affected by the grain boundaries. The mode-specific phonon transmission coefficients can be recovered by fitting the BTE-simulated MFP spectrum to the measurements. The variance reduced Monte Carlo algorithm introduced in Chapter 2 could be used to simulate the thermal transport. Rather than a simple 3D grain structure used in this work, one could extend the simple structure to the real structures as characterized by the transmission electron microscopy.

Superlattices, a periodic structure of layers of two or more, are another materials of great interests though little is known about microscopic phonon transport processes in them. A similar study on the interfacial heat transport as done in Chapter 5 could be carried out after one extends the two-layer BTE solution to include multiple layers.

Next, more attention is worth drawing to further explore the energy transport in the transition regime between ballistic and diffusive propagation. This regime holds valuable information on the nature of energy carriers in solids. Our work has identified two sub categories within this transition regime, demonstrating that this transition regime might be more complicated than previously understood. Other recent

work(*182*) has demonstrated that there might be another new regime where heat dissipation efficiency could be enhanced even when characteristic length are much smaller than the energy carriers' MFPs. A comprehensive picture of nanoscale energy transport is not only necessary but also crucial to achieve precise control of heat in solids.

Besides phonons, electrons also play a crucial role in energy transport in metals and semiconductors. Electron and phonon coupling is ubiquitous in condensed matter. Electron scattering by phonons is one of the major processes which determines the transport characteristics in metals and semiconductors. With the advance in first-principle calculations, it is now possible to get the spectral properties of electrons in both metal and semiconductor-based materials, which provides inputs for electron transport modeling. As previously done for phonon transport, one can rigorously investigate the electron-phonon interaction in semiconductor/metal-based materials using the combination of ab-initio transport modeling and ultrafast optical techniques done previously for phonon transport.

These are just a few of the possibilities which could yield important and useful information about nanoscale energy transport. Energy manipulation at the nanoscale is at the forefront of modern technological innovation, and our understanding of energy transport at this scale would lead to more robust and efficient methods of designing frontier materials and devices. We hope this thesis has given insights into microscopic processes of energy carriers in solids and will be useful for achieving our ultimate goal of energy manipulation.