論文の内容の要旨

論文題目　Simulation of decoupled thermal and electrical transport in silicon nanostructures
(熱と電子の輸送を独立制御するためのシリコンナノ構造の数値解析)

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1. Introduction

Heat transfer at nanoscale is significantly different from that in macroscales because of the strong size effects on electron and phonon transport. Nanoscale heat transfer finds great interests in various areas such as microelectronic industries, thermal management, device design and active cooling. One of the most exiting applications may go to thermoelectric technology, which is capable of converting waste heat energy directly into electricity. Its efficiency is gauged by the dimensionless figure of merit: $ZT= S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity composing of both lattice and electronic parts [1]. The reduction of heat is strongly beneficial for the enhancement of conversion efficiency of thermoelectrics. In fact, the entangling mechanism of those physical quantities has made the search of highly efficient thermoelectric materials quite difficult.

Last a few decades have seen great efforts in reducing lattice thermal conductivity of semiconductor materials to enhance ZT [2,3]. One of the most important strategy is nanostructuring. The main conception is either sufficient gain from electron properties facilitated by low-dimensional electron confinement effect, or drastic suppression of thermal conduction due to nanostructure itself. It offers a solution to relieve the contradiction of the intertwined thermal and electrical transport for thermoelectrics. Especially, much attention goes

to silicon, whose charming points as potentially good thermoelectrics can be raised as environmental-friendly, abundant and cost-effective. Therefore there is enormous interest of tuning Si towards a good thermoelectrics by reducing lattice thermal conductivity via nanostructures.

There has been great efforts in fabrication of Si bulk nanostructures with *ZT* enhancement based on bottom-up approach such as sintering Si nanoparticles [4,5]. With downsizing to several nanometers in experiment, on contrary to the conventional bottom-up approach, a delicate control of morphology and composition of nanostructures at atomistic level becomes highly accessible [6-8]. This opens another door to search for the optimally effective nanostructure to separately control mean free path of phonon and electron, so-called decoupling thermal and electrical transport, to realize Si nanostructure design for high *ZT* value. It is thus highly desirable that the numerical simulations at atomistic level could offer valuable insights into the idea of decoupling by digging up several such effective nanostructures. In this thesis, we demonstrate the idea of decoupled thermal and electrical transport for the purpose of *ZT* enhancement in the system of Si matrix embedded with different nanoinclusions by numerical simulations. In this way, we try to come up with common ideas in terms of morphology control and structural design in such system for realizing effective decoupled thermal and electrical transport to enhance *ZT* value.

2. Methodology

We review in this chapter the computational methods we employ in this study for both phonon and electron transports. For phonon part, we briefly introduce first-principles based microscopic thermal transport analysis, molecular dynamics for model construction, phonon wave-packet method for the phonon wave scattering phenomenon, and atomistic Green's function for phonon transmission evaluation. For electron part, we focus on non-equilibrium Green's function method for electron transmission calculation, and the rudiment of tight-binding model. The method of evaluating *ZT* that are realistic and directly comparable to experiments are made possible by incorporating diffusive transport treatment into the ballistic evaluation of elastic nano-inclusion scattering.

3. Morphology exploration of nano-silica in Si matrix for *ZT* enhancement

We firstly focus on the system where silica (amorphous SiO_2) is embedded in Si matrix, termed as Si/α-SiO_2, and it holds ubiquitous meaning for Si industry since the natural or artificial oxidation of Si would easily result in such system. Sakata *et al.* [6] have successfully made a planar interface by sintering two planar materials of Si that allow to study the effect of a clean interface. The effect of crystal orientation, sintering temperature, and inclusion of oxidized Si on thermal boundary conductance of the interface has been investigated in detail.

They clarify that inclusion of oxidized Si at the Si-Si interface would yield controllability of an order of magnitude of thermal boundary conductance. This offers valuable insights into the design index for interfacial thermal transport for nanostructuring Si. However, the electrical properties remain unknown.

Considering its insulator nature, the challenge for realizing decoupled thermal and electrical transport lies in the severe degradation of electrical performance. We thus propose a precise morphology control which would retain its electrical performance. The cross-section density of α-SiO_2 is found to overwhelmingly affect both thermal and electrical transport in that, there is a range of cross-section density that would realize an valid decoupled transport leading to enhancement of *ZT*, out of which the electrical performance deteriorates rapidly and thermal reduction reaches plateau, i.e., an very adverse regime for enhancement. Moreover, shape, characteristic size of α-SiO_2 and inter-particle distance between them are also found to affect the electrical performance, and those parameters can be adjusted further for optimal *ZT* given a plausible value of cross-section density, say 0.05~0.25. The final gain in *ZT* at 300 K is estimated to be about two times that of pure Si single crystal, which is a conservative value and comparable to that of Si polycrystalline.

4. Phonon-interference resonance effects and *ZT* enhancement of Ge nanoparticles embedded in Si matrix

We demonstrate in this chapter by another system where germanium (Ge) nanoparticles are embedded in Si matrix, termed as Si/GeNPs. Yamasaka *et al.* [7] have recently reported a novel structure where Ge nanodots are coherently embedded in Si matrix. The very thin Si oxidation film is also present in the structure, together with Ge nanodots, contributing to a low thermal conductivity. The reported value is 1.2 $Wm^{-1}K^{-1}$ for diameter of Ge nanodots are 5 nm and the volume fraction of Ge is only 12%. This value outperforms those with equivalent amount of Ge element of bulk Si/Ge nanostructured thermoelectrics. Moreover, after suitable doping they have even managed to achieve an enhancement of *ZT* [8]. Meanwhile, the individual Ge nanoparticles can be considered as local phonon resonator interacting with phonons with long wavelength, and it is thus quite interesting to investigate the possible resonance effects of Ge nanoparticles that could potentially block phonons with long wavelength and lead to thermal transport reduction.

Si/GeNPs is a novel system that it requires a precise fabrication control to realize a coherent lattice connection between GeNPs and Si matrix. This in turn facilitates a smooth flow for electron and removes the stringent issue of morphology control since Ge has similar electrical properties as Si and is conductive. The realization of decoupled thermal and electrical transport here thus lies in further thermal reduction. We identify an unambiguous phonon resonance

effects originating from GeNPs interacting with phonon waves, leading to a resonant reflection of the lower-end phonons with very long wavelength, and it helps reduce their contribution to thermal conduction. The impact of resonance can be magnified by installing multiple layers of GeNPs due to the superposition of the resonant reflection and collective motion. We also clarify different particle shapes can selectively generate resonance with different resonant frequency and transmittance profile. A combination of different size, shapes of multiple GeNPs can thus realize a synergetic resonance effect that leads to more substantial thermal reduction. The effect of phonon coherence length on resonance is studied, and it indicates a very long coherence length, or a true-nano-scale particle is required to assure a complete resonant reflection, otherwise a deteriorated one. The finding holds universal importance in many phonon wave related phenomena such as interference and resonance. The final gain in *ZT* at 300 K is estimated to be about five times that of pure Si single crystal.

5. Conclusions

The thesis demonstrates that Si matrix dispersed with nano-inclusions with a precise control of embedded structure/interface can be a promising system for *ZT* enhancement by a decoupled thermal and electrical transport, together with the conventional bottom-up approach for polycrystalline. We get common ideas in terms of morphology control and structural design in such system for realizing effective decoupled thermal and electrical transport to enhance *ZT* value. If the nano-inclusion is insulator-like, a stringent morphology control would be required to retain its electrical properties as the scenario for Si/α-SiO_2. If it is conductive-like, approaches such as phonon resonance that leads to more thermal reduction is encouraged to be employed as the scenario for Si/GeNPs. Apart from GeNPs, we consider other metal nanoparticles whose morphology can be controlled at atomistic level can be a good alternative. This study, being a numerical simulation, contributes to the understanding of decoupled thermal and electrical transport in Si nanostructures for *ZT* enhancement.

Reference

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