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博士論文 (要約)

**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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Thermoelectrics is becoming one of the most important and promising energy-harvesting technology that help mitigate the great challenges such as climate changes, rapid exhaustion of non-renewable energy resources. Thermoelectric materials could convert waste heat energy directly into electricity, one of the most important primary energy resource in our life. In such way, it collects large amounts of waste heat, which is one of most common energy losses and ubiquitous energies at the same time in our world, and convert them into clean electric energy. Therefore thermoelectrics holds significantly large social impacts and reckoned as one of the pillar technologies for next-generation low-carbon society.

In the past decades, there have been enormous efforts discovering and fabricating high efficiency thermoelectric materials, which is gauged by the non-dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is electrical conductivity, and  $\kappa$  is thermal conductivity composing of both lattice and electronic parts. The efforts have been devoted to reach a delicate balance of thermal and electrical performance in materials at the same time, i.e., low thermal conductivity while high power factor ( $S^2\sigma$ ). It has been proven that such relationship is mostly likely to happen and is promising to be manipulated in semiconductors instead of metal or insulators. It is no wonder that several high efficiency thermoelectrics stereotypes belong to this group, such as  $\text{Bi}_2\text{Te}_3$ ,  $\text{PbTe}$  and  $\text{SiGe}$ -alloy. It is worth noting that 1993 has witnessed a big breakthrough of enhancement of  $ZT$  value in theory. Hick and Dresselhaus have predicted that low-dimension would enhance  $ZT$  by decreasing thermal conductivity and maintaining (or increasing) electrical conductivity simultaneously. Afterwards the idea has been proven by numerous experimental reports, which bring large excitements to the thermoelectrics community. The most favorable realization of low dimension is to make nanostructures, especially those called bulk nanostructures, which bears impact from pragmatic viewpoint. The effectiveness of nanostructures to lead to high  $ZT$  lies in the possibility of scattering phonons, which is quantized lattice vibration in semiconductors and is responsible for thermal conduction, prior to that of electrons. This helps restrict the phonon mean free path (MFP, the mean path of one particle traveling before colliding with other particles) to the characteristic size of the nanostructure, an appreciable decrement from several  $\mu\text{m}$  to  $\text{nm}$  order, thus decreasing thermal conductivity, whilst the electron MFP is usually much smaller than the size of the nanostructure and less affected and scattered. Nanostructure proves to be powerful way to tune Silicon (Si) into high efficiency thermoelectrics because of the reasons above, otherwise it is quite a poor one due to the high thermal conductivity. People hold large interest in Si because of its abundance and non-toxicity, cost-effectiveness and compatibility with current Si technology. Several noteworthy experimental achievements for bulk-nanostructuring Si includes from conventional bottom-up approach of sintering Si nanoparticle of nano-order

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size to a bulk plate, to novel molecular beam approach with well-controlled particle size and compositions.

With downsizing to several nanometers in experiment, a delicate control of morphology and composition of nanostructures at atomistic level becomes highly accessible. This opens another door to search for the optimal effective nanostructure to separately control MFP of phonon and electron, so-called decoupling thermal and electron transport, to realize nanostructure design for high ZT Si thermoelectrics. 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 propose two systems for demonstrating the idea of decoupling and show their possibilities of enhancing ZT value. In this way, we try to come up with common ideas of nanostructure design for high ZT Si thermoelectrics.

For further reduction of thermal conductivity, the key is to inhibit transport of phonons with the lower-end frequencies (from sub THz to a few THz) because they tunnel through the interface (grain boundary) since the transmittance asymptotically approaches unity as frequency decreases. The exact critical frequency below which the tunability becomes impacting depends on the material, but for instance a recent study on crystal-amorphous silicon (Si) nanocomposite has shown that phonons with frequency below a few THz still propagate and contribute to a large fraction of the remaining thermal transport. Such significance of phonons with the lower-end frequencies should be applicable in general for nanostructured crystalline materials with low thermal conductivity.

A widely explored approach to impede low frequency phonons is to construct a phononic crystal, which inhibits propagation of phonons within certain frequency range as a consequence of interference of phonon waves reflected at the periodic structures. A challenge from practical viewpoint lies in the necessity to pattern the periodic structures at the nanoscale such as the epitaxial superlattices. Although top-down nanofabrication (such as holes) with length scale of  $\sim 100$  nm is possible, the target phonon frequency would be limited to the order of gigahertz, which has negligible contribution to thermal transport at room temperature due to the small density of states.

One way to introduce phonon interference without having to construct spatially periodic structures is to exploit local resonance. This has been theoretically demonstrated in various systems with the “added-structures” such as nanowires and thin films with pillars erected on the surface, and a solid interface with embedded defect-atom arrays. The effect of local resonance on reflection enhancement can be related with destructive interference of different phonon paths in real space (through and around the local resonator), and results in flattening of phonon bands or in total reflection of phonons at certain frequencies. However, to impact

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phonons with the lower-end frequencies, the above “added-structures” need to be built at the nanoscale, and thus would still be extremely challenging.

We conduct polarization-wise phonon wave-packet (PWP) simulations based on molecular dynamics (MD) of both longitudinal and transverse acoustic (LA and TA) waves to retrieve the resonance frequencies, transmittance, and associated vibrational mode of the GeNP and highlight the impact of coherence length on resonance effect. We ensure the same area fraction ( $\pi d^2/4w^2$ ) of the spherical GeNPs when varying their diameters  $d$  and side lengths of the square cross section  $w$ . The relation of the local resonance in GeNP with the classical problem of dynamic deformation of an elastic particle embedded in a matrix is highlighted through the analysis of vibrational eigenstates with finite element method (FEM) based on continuum theory. Possibilities to enhance resonance reflection is discussed by varying coherence length of PWP and forming an array of GeNPs for collective modes. Finally impact of the resonance effect on thermal transport is quantified by atomistic Green’s function (AGF) method calculating frequency  $\omega$  dependent spectral thermal conductance  $G(\omega)$ .

There have been constant endeavors to tune bulk Si towards a highly efficient thermoelectric materials. The most efficient way to make nanostructured materials to decouple the electron and phonon transport, i.e., taking advantage of the difference in their mean free path, to realize priori scattering of phonons and less scattering or maintain of electrons. Several exciting experimental achievements have been reported, including conventional bottom-up approaches that sinter Si nanoparticle to form bulk plate, and novel techniques such as molecular beam epitaxy to realize precise morphology control even at atomic level.

Yamasaka et al. used the same molecular beam epitaxy technique to fabricate nanoparticle-matrix system where Ge nanodots with several nanometer embedded in Si matrix. The oxidized thin films are found to be present during the fabrication process and thought to be inevitable. Together with Ge nanodots that scatter phonons, such structure also realize low thermal conductivity as low as  $1.2 \text{ Wm}^{-1}\text{K}^{-1}$  with quite small amount of Ge. It is demonstrated that upon suitable doping that recovers its electrical properties, such structure could achieve a enhancement of ZT. In last chapter, we focus on the similar system where Ge nanoparticles are coherently embedded in Si matrix, and study the phonon-interference resonance effects of Ge nanoparticles and reveal its strong impact on blocking the transport of lower-end frequency phonons. We note that even though the structure with Ge nanoparticles is quite promising and can be further tuned to achieve better performance, introducing Ge in Si still entails uncertainties such as diffusion of Ge atom into Si lattice. On the other hand, the oxidized Si thin film, i.e.,  $\text{SiO}_x$  is almost inevitable and is a very natural substance during Si operation process. If we could achieve delicate control of nanostructure that contains  $\text{SiO}_x$  and tune it

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towards highly efficient thermoelectrics, the social impact would be extremely large and quite useful for Si industry. As its counterpart in experimental fabrication, it also calls for simulation at atomistic scale to provide deep insights into effective decoupling of electron and phonon transport. Such object-oriented design for materials is becoming more and more important in searching for highly functional materials.

We demonstrate that nano-silica in Si matrix is possible approach to enhance ZT performance by decoupling electron and phonon transport. The ZT value is optimized when the reduction of electron and phonon transport reach a delicate balance that phonon transport is suppressed and the electron transport is maintained.

We conclude that morphology of nano-silica is of critical importance in tailing such delicate balance, and actually this is the advantage of such nanostructure that current experimental techniques have enabled atomistic-level manipulation of structures. We consider several factors governing morphology of nano-silica that are of particular importance. Firstly the cross-section density is important in that it has a threshold, above which the electron transmission, or the electrical performance decreases heavily. Based on current simulation results, we conclude that best cross-section density should be around  $1/4$ . Another important factor is the length along the transport direction. Large length would deteriorate the electrical conductivity, but possibly lead to a high Seebeck coefficient. The length along the transport direction should not be longer than 0.7 nm. The third factor is characteristic size of nano-silica. We conclude the small size  $\sim 0.5$  nm is favorable to high hole transmission near the valence band edge and a large size (no smaller than 1.1 nm) is good for electron when they have the same cross-section density. Ultimately, the small and dense nano-silica are considered to be efficient for enhancement of *ZT*.