Investigation on transport properties in nanowires with contacts

Li, Jing

2012

Li, Jing. (2012). Investigation on transport properties in nanowires with contacts. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54730>

<https://doi.org/10.32657/10356/54730>

INVESTIGATION ON TRANSPORT PROPERTIES IN NANOWIRES WITH CONTACTS

LI JING

School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2012

ACKNOWLEDGEMENTS

I am full of gratitude to my supervisors, Prof. Kam Chan Hin and Prof. Au Yeung Tin Cheung for their thoughtful guidance, planning and support to enable the progress of this project, without which none of this work would ever have been possible. I appreciate greatly their trust and constant encouragement.

I am especially grateful to Dr. Quan Jun, Dr. Yu Yabin, Dr. Zhao Xuean and Prof. Sun Chang Qing for their selfless help in this project. They had imparted the important knowledge in modeling and had dedicated their time in answering many of my queries.

I would like to express my gratitude to my family, especially my parents and wife, for their supports.

I would like to thank my labmates, Lin Shihuan, Liu Yangjie, Srikanth Kamakshi Machavolu, Wu Xing, Yan Yafei, Zhang Xi, Zhang Junbing, Zhu Guojun and Zhu Yinbing, in Computational Nano-electronic Lab for fruitful discussions and sharing their experience.

TABLE OF CONTENTS

DEDICATION	iii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	ix
I INTRODUCTION	1
1.1 Motivations	1
1.1.1 The shrinkage of the transistor	1
1.1.2 The efficiency of thermoelectric device	2
1.2 Scope	3
1.2.1 Phonon transport	4
1.2.2 Electron transport	5
II LITERATURE REVIEW	6
2.1 Phonon Transport	6
2.1.1 Thermal Energy	6
2.1.2 Phonon	7
2.1.3 Lattice Vibration	10
2.1.4 Phonon Transport	12
2.2 Electron Transport	16
2.2.1 Semi-classical approach	17
2.2.2 Non-equilibrium Green's Function Method	21
III EFFECT OF SURFACE BOND RECONSTRUCTION ON THE CONTACTS: PHONON TRANSPORT IN SILICON ATOMIC WIRE	28
3.1 Theory	29
3.1.1 Modeled System Description	29
3.1.2 Lennard-Jones potential with SBR effect	30
3.1.3 Dynamical matrix of thermal contact	33

3.1.4	Green's function at contact surface	35
3.1.5	Self-energy of LD and RD regions	37
3.1.6	Green's Function of whole wire	38
3.1.7	Equilibrium Assumption in LD and RD Regions	39
3.1.8	Green's function with anharmonic effect	40
3.2	Effect of surface bond reconstruction	41
3.2.1	Phonon density of states	42
3.2.2	Phonon transmission	44
3.2.3	Thermal conductance by phonon	45
3.2.4	Passivation of dangling bonds	46
3.2.5	Local currents in LD region	46
3.2.6	Variation in length, coupling strength and stiffness	47
3.2.7	Anharmonic effect in the wire	50
IV	PHONON TRANSPORT IN SILICON NANOWIRE: SIZE AND DOPING	56
4.1	Theory	56
4.2	Result	60
4.2.1	Density of states	60
4.2.2	Size dependence	61
4.2.3	Site dependent of Ge atom substitution	65
4.2.4	Conclusion	69
V	PHONON TRANSPORT IN GOLD WIRE WITH BUFFER LAYER 70	
5.1	Theory	70
5.1.1	Model description	70
5.1.2	Embedded atom method (EAM)	71
5.1.3	Green's function and conductance	73
5.2	Results and Discussions	76
5.3	Conclusion	80

VI ELECTRON TRANSPORT IN THERMOELECTRIC DEVICE	81
6.1 The importance of electronic thermoelectric efficiency	81
6.1.1 Power flow in TE device	82
6.1.2 Reformulate figure of merit	85
6.1.3 Two upper limits of FOM	87
6.1.4 TE device with rectangular transmission function	87
6.1.5 Thermoelectricity in silicon nanowire	88
6.1.6 Conclusion	95
6.2 Scattering effect on thermoelectricity	96
6.2.1 Introduction	96
6.2.2 Model	96
6.2.3 Discussion	99
6.2.4 Conclusion	106
6.3 Field effect thermoelectric device	106
6.3.1 Device Description	106
6.3.2 Simulation and discussion	107
6.3.3 Conclusion	111
VII CONCLUSION	112
7.1 Perspectives	112
7.1.1 Phonon transport	112
7.1.2 Electron transport	113
7.2 Summary	113
APPENDIX A — PUBLICATION LIST	116
REFERENCES	118

LIST OF TABLES

1	Parameters of gold [61]	75
2	Symbols used in thermoelectric effect	82
3	Parameters of Silicon [103, 104]	90

LIST OF FIGURES

1	Modeled system of phonon transport, a two-probe system.	14
2	Modeled System: An atomic wire coupled by two semi-infinite silicon thermal contacts.	30
3	Whole Atomic Wire: The whole atomic wire, LD and RD regions are set to be one unit cell of silicon crystal.	31
4	First Brillouin zone and unit cell of (0,0,1) surface in F.C.C crystal structure.	34
5	Conversion of semi-infinite thermal contact to saw-tooth atomic chain. . . .	35
6	Density of states for a) bulk Si, b) first atomic layer, c) second atomic layer, d) third atomic layer. The solid line corresponds to the case without surface bond contraction, and the dashed line corresponds to the case with surface bond contractions at the Si contact surface.	43
7	Transmission function for the case, that is, both the regions LD and RD are in thermal equilibrium. (a) Total transmission function, (b) Contribution of $\vec{k}_{ } = 0$ to transmission function, (c) Contribution of $\vec{k}_{ } = \frac{\pi}{a}(0, 0.5)$ to transmission function, (d) Contribution of $\vec{k}_{ } = \frac{\pi}{a}(0.5, 0.5)$ to transmission function. 'a' is the lattice constant for Si.	44
8	Thermal conductance in a Si atomic wire due to phonon transport.	46
9	Local heat currents between any two atoms in the region LD for a) the case of no SBR, and for b) the base of SBR. The magnitude of the local heat currents are represented by red color: slight red means weak current and deep red means strong current.	47
10	Thermal conductance with various atomic wire length. Result is obtained under the condition, $t_m = 0.316 \text{ eV}/\text{\AA}^2$, $t_{r,l} = 3.16 \text{ eV}/\text{\AA}^2$ and $T = 300 \text{ K}$.	48
11	Transmission probability with $t_m = 0.316 \text{ eV}/\text{\AA}^2$, $t_{r,l} = 3.16 \text{ eV}/\text{\AA}^2$, the highest frequency is around 21 THz.	49
12	Thermal conductance with the change of coupling between the wire and silicon surface, with fixed $t_m = 1 \text{ eV}/\text{\AA}^2$	50

13	(a) Relative decrease in thermal conductance of the atomic wire due to anharmonicity, as a function of temperature, (b) Thermal conductance of the atomic wire due to the harmonic approximation of the Lennard-Jones potential, as a function of temperature, (c) Thermal conductance of the atomic wire in the presence of anharmonicity, as a function of temperature, (d) The thermal conductance σ_1 calculated from the first term of Eq.128, as a function of temperature, (e) The thermal conductance σ_2 calculated from the second term of Eq.129, as a function of temperature.	52
14	(a) Transmission function at temperatures $T = 100$ K in the absence of SBR, as a function of frequency. The dashed line corresponds to the presence of anharmonicity, and the solid line corresponds to the harmonic approximation of the Lennard-Jones potential, (b) Transmission function at temperatures $T = 100$ K in the presence of SBR, as a function of frequency. The dashed line corresponds to the presence of anharmonicity, and the solid line corresponds to the harmonic approximation of the Lennard-Jones potential. (c) and (d) Similar to (a) and (b), with $T = 400$ K.	54
15	(a): Schematic diagram of the modeled system: a Si nanowire connected to two semi-infinite Si contacts, the parts LD and RD inside contacts are included into the wire. (b): Distribution of atoms for SiNW with $w = a$ and $l_z = 3a$. Both LD and RD region have 9 atoms.	57
16	Phonon density of state for bulk Silicon. Insert: the dispersion relation. . .	60
17	Phonon density of states for surface plane and the plane deep inside contact (treated as bulk case).	61
18	Phonon DOS of square shaped silicon nanowires with side length $1a$, $2a$, $4a$ and $6a$. ($a = 5.4309$ Å)	62
19	Phonon transmission of square shaped nanowires with length $3a$. The legend denotes the side length of the cross-section of the nanowires.	63
20	Thermal conductance of squared wire with various side lengths respect to temperature in (a): log scale, (b): linear scale.	64
21	Thermal conductance (Dash Line) and Thermal conductance density (Solid Line) change with cross-sectional area of square shaped SiNW.	65
22	Four types of atomic layer (cross-section view) in SiNW with $w = 1a$. Number of bonds are indicated for each atom.	66
23	Phonon transmission function of SiNW. (a) pristine SiNW; (b) Same as (a) except the scale of the frequency is divided by a factor of 1.64. (c) All atoms which are allowed to be substituted, are substituted by Ge atoms.	66

24	(a): Percentage changes in thermal conductance with different Ge content. Maximum, Mean and Minimum line denotes the variance of thermal conductance. Dash line represents bulk Si-Ge alloy using the data from J.Garg's work[83]. (b): Percentage change in thermal conductance due to single Ge atom substitution with change in z for 3 groups of bond numbers for the substituted atom.	67
25	A typical configuration of thermal transport systems. The smaller figure shows the cross section viewed from $[010]$ direction.	71
26	Cases of different number of atomic layers N in the buffer layers, view from $[010]$ direction.	72
27	a) The direct lattice unit cell in the contact surface, and b) the first Brillouin Zone. a_0 is the lattice constant	75
28	a) Bulk density of state of contact, b) Surface densities of states. Blue dashed line is DOS of $g_{xx}(\omega)$ or $g_{yy}(\omega)$ parallel to the contact surface. Red solid line is DOS $g_{zz}(\omega)$ perpendicular to the contact surface.	76
29	The solid lines are DOS of finite atomic chains (7 atoms) for structures a), b), c) and d) in Fig.26. The dashed line in plot A is DOS of the infinite atomic chain.	77
30	Thermal conductances of different junction configurations. The numbers indicate the structures corresponding to Fig.26. Inset are thermal conductance as a function of buffer layer number N at Debye temperature and low temperature thermal conductance, respectively.	78
31	Transmission probabilities corresponding to system a), b), c) and d) in Fig.26	79
32	(a): Figure of merit ZT is mapped by A and ξ , where A is the ratio of thermal conductance by phonons K_l over the electronic thermal conductance K_p , and ξ is the electronic thermoelectric efficiency. To achieve $ZT > 1$, the condition $\xi > 0.5$ and $A < 1$ is necessary. (b): Power flow diagram in a thermoelectric device: among the three powers (P_{K_l} , P_{K_e} and P_{TE}), only P_{TE} is used to generated electricity. The expressions ($\frac{1}{A+1}$, $\frac{A}{A+1}$, ξ and $1 - \xi$) indicates the fraction of power flow. (c): The directions of electric current and heat current due to temperature gradient in thermoelectric device at 300 K. Opposite flow direction in electric current for the components above and below Fermi level, result in the reduction in thermoelectric effect.	84

33	(a): Rectangular shaped transmission function with center located at E_c , energy width ΔE and transmission β ; (b): Normalized K_p (electronic equivalent thermal conductance); (c): ξ (electronic thermoelectric efficiency), and (d): Normalized $(K_p \cdot \xi)$ with various ΔE and E_c . The optimal region for the rectangular thermoelectric device is bounded by the contour line 0.99 in (d), which is also plotted in (b) and (c), as indicated by E_{op}	89
34	Electron density of states (DOS) in the conduction band ($E - E_c$) of Silicon nanowires with length 10 μm and various diameters (5 nm, 10 nm, 30 nm and 50 nm).	91
35	Fermi level relative to the bottom of the conduction band ($\mu - E_c$) in Silicon nanowires with the change of N-type doping concentration N at 300 K.	91
36	(a): The Seebeck coefficient S , (b): Electric conductivity σ , (c): Thermal conductivity by charge carriers κ_e , and (d): the relative error of Wiedemann-Franz law $(\kappa_{WF} - \kappa_e)/\kappa_e$ of Silicon nanowires with the change of N-type doping concentration N at 300 K.	92
37	(a): Electronic thermoelectric efficiency ξ , and (b): Electronic equivalent thermal conductivity κ_p with the change of N-type doping concentration N at 300K. The circle indicates the optimal region for figure of merit, where the Fermi statistics transit from non-degenerate to degenerate.	94
38	Figure of merit ZT of Silicon nanowires with N-type doping concentration 10^{18} cm^{-3} at 300 K. The limit 1 and limit 2 are determined by Eq.(178) and Eq.(179), respectively.	94
39	The schematic of the modelled system: a nanowire coupled by two contacts at both ends, the scattering points denoted by the square box is coupled to Büttiker probe through a virtual contact.	97
40	The electron density in a nanowire with the length 18 nm, two scattering points are inserted at the $z = 6 \text{ nm}$ and $z = 12 \text{ nm}$, (a) is for the weak scattering and (b) is for the strong scattering. α is the scattering strength.	101
41	A 9 nm nanowire with the presence of biased voltage ΔV , (a): the electron density, and (b): the electrical current in weak scattering condition; (c): the electron density, and (d): the electrical current in strong scattering condition. α is the scattering strength.	102
42	A 9nm nanowire with the presence of various biased voltages, the electrical current with the change of scattering strength α	103
43	A 9nm nanowire with temperature difference ΔT , (a): Seebeck coefficient, and (b): electrical conductance in weak scattering condition; (c): Seebeck coefficient, and (d): electrical conductance in strong scattering condition. α is the scattering strength.	104

44	A 9nm nanowire with temperature difference ΔT , the thermoelectric power factor with the change of scattering strength α with (a): small temperature difference, and (b): large temperature difference.	105
45	(a): The schematic of proposed device: two metal parts are connected by semiconductor thin films, between which gates and dielectric layers are inserted. (b): Band diagram of n-type leg with positive gate voltage applied. Region A, B and C refer to metal, uncovered region and covered region. . .	107
46	The proposed device with $V_g = 0.08$ eV. (a): The electron transmission function. Electrons transmission below E_f are blocked by barriers. (b): Electron density of states are shifted to lower energy due to the positive gate voltage.	109
47	Related parameters to TE effect at 300 K, with various gate voltages. (a): Figure of merit ZT ; (b) Thermal conductance by electron K_e ; (c) Electric conductance σ ; (d) Seebeck Coefficient S	110

CHAPTER I

INTRODUCTION

1.1 Motivations

1.1.1 The shrinkage of the transistor

Since the invention of the transistor, the fundamental element of the integrated circuit (IC) in 1960s, with the revolution in semiconductor industry, the transistor size has been getting smaller every year. Due to this reason, the number of transistors on a single IC chip increases following Moore's Law, electronic devices are able to provide more advanced and complex functionality with higher effectiveness. Therefore, the advancement of semiconductor technology is measured by the size of the smallest transistor possible to be fabricated.

When the transistor size goes down to hundreds of nano-meter, it enter the sub-micrometer scale, rather than nano-meter scale. This is because, the physics in the transistor with sub-micrometer scale is similar to that in micrometer scale. Therefore, the existing IC design concepts and fabrication processes in micrometer scale can be easily transferred to the semiconductor technology in sub-micrometer scale, and this is the reason behind the continuity of development in semiconductor technology. The transistor size was 180 nm in year 1999, and was 32 nm in year 2011.

When the transistor size become tens of nano-meter or even a few nano-meters, the distance between two atoms (normally 2 to 5 Å with Å equals to 10^{-10} meter) is comparable to the transistor size. The disappearance of the periodicity of atoms in certain directions leads to low dimensional device (thin film, nanowire and quantum dot). Surface effect and non-local effect are so strong that the physical properties of the semiconductor material which is used to fabricate the transistor, in this scale

is very different from that in the bulk size. The transfer of existing design concepts and fabrication processes to this scale does not work any more. Investigation of the physical properties of nano-structure becomes a crucial task.

Transistors are designed based on the charge transport property. An external gate voltage is used to control the conductance of the channel between the source and the drain; with that the electric signal is able to be manipulated. In nano-scale device, the contact interfaces between the channel and the reservoirs, which can be the source or the drain, plays an important role in the transport properties. This effect can be studied systematically in the two-probe systems. In an electronic device, the dissipation of the heat generated by Joule heating is important to the reliability and the life time of the device and is governed by the thermal transport property.

1.1.2 The efficiency of thermoelectric device

Energy and environmental problems are great challenges to human society. Today, 90% of the energy we use is from carbon-based non-renewable fossil fuel. The exhaust gases pollutes our environment heavily. Furthermore, the efficiency of our current heat engine is quite low. Up to 60% of a gasoline engine's energy is lost through waste heat [1]. That means that only 40% of the millions of ton of fossil fuel we burn every year is useful. In this manner, fossil fuel will be exhausted soon, and the planet will be highly polluted. A possible solution to energy and environmental problems is the use of thermoelectric devices to harvest electrical energy from waste heat. A thermoelectric device is a solid state device without moving parts, thus it is almost maintenance-free. It is a clean device as there is no exhaust gas and thus not harmful to the environment. In the long term, the development of highly efficient thermoelectric generator (TEG) will drive up the efficiency of other structures and can be used in addition to other approaches of green energy.

In recent years, the development of thermoelectric devices has received a lot of

attention. Many research groups focus on improving the thermoelectric characteristics of materials. Although this research has led to better thermoelectric materials, there is not much progress in putting thermoelectric devices to wide practical use. The reason behind this is the relatively high economical cost. Currently, thermoelectric devices are used in high end industries, for example in space probes. But there is evidence that thermoelectric devices could become part of our daily life. For instance German automakers Volkswagen and BMW have developed thermoelectric generators (TEG) that convert waste heat from a combustion engine. The engine is able to produce electricity, which meets 30% of the car's electrical requirements, resulting in a reduced mechanical load and a reduction in fuel consumption of more than 5%. Based on this, we predict wide use of thermoelectric devices in 5 to 10 years. To realize this, thermoelectric devices need a boost in efficiency to reduce their effective economical cost.

The efficiency of a TE device is measured by the dimensionless TE figure of merit (FOM), which is intimately related to the charge and thermal transport properties. Researchers have been searching for high FOM TE device for over 50 years. In 1960s, alloys of Bi_2Te_3 were reported with FOM of about one [2]. Thereafter, the progress was very slow until recent years, when TE device with FOM greater than one were reported [3, 4, 5]. With the development of technology, TE device can be made on the nanoscale [1, 6], which increases the feasibility of engineering the transport properties. The sharp structure of the electron density of states in nano-structures [7] provide opportunities for boosting FOM [8].

1.2 Scope

With the motivations of investigating the transport properties in nano-structures, we embark on this research. The transport properties discussed in this work are the charge transport and the thermal transport, which are categorized by the effect of the

transport, (i.e. in the charge transport, electric charges are transferred; while in the thermal transport, thermal energy is transferred), or in terms of electron transport and phonon transport, which are categorized by the particle transferred, (i.e. in the electron transport, electrons are transferred; while in the phonon transport, phonon is transferred. The electrons transport contributes both to the charge transport and the thermal transport, but the phonon transport contributes only to the thermal transport.

1.2.1 Phonon transport

Much attention has been focused on the phonon properties of nano systems in recent years due to their great importance in fundamental low-dimensional physics as well as in applications of nano-scale devices[9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. With the development of non-equilibrium Green's function in phonon transport, a systematic and effective way is provided to study phonon transport in nano-structure and to determine the physical quantities, such as density of state, transmission probability, thermal conductance, etc.. The detailed formulation of non-equilibrium Green's function is introduced in the literature review of phonon transport (section 2.1).

In a system where two thermal contacts are connected by a nano-structure, the surface bond reconstruction (SBR) of the thermal contacts affects phonon transport significantly. This is because, around the surface of thermal contact (normally the first few layers), bond strength and inter-atomic distances are substantially different from the bulk case. Therefore, the inter-atomic forces near the surface of thermal contact are significant changed. Due to this reason, phonon density of states at contact surface is modified, which brings a dramatic change in thermal conductance. Another important factor affecting phonon transport is the nonlinear interaction between atoms in an atomic wire. Nonlinear effect causes scatterings in ballistic phonon transport and affects the thermal conductance. However, this effect is ignored in most

of the previous works, which motivates our interest in studying it. In chapter 3, the effect of SBR and anharmonicity are discussed [19, 20, 21].

Contact interface always plays an important role in nano-scale phonon transport. This is because phonons undergo reflections when they go through the contact interface. Besides the effect of SBR on thermal contact, we also studied the effect of buffered layer. The phonon transport properties of the system, in which pyramidal regions (treated as buffered layers) are inserted between the contact surface and atomic wire, are discussed in chapter 5[22].

Generally, a good TE device is one with a small phonon conductance. Recent research shows silicon nanowires have good potential in achieving high TE efficiency. To reduce the phonon conductance, substitution of silicon atoms with germanium atoms is an effective way. In chapter 4, we studied the phonon transport in silicon nanowires with the variation of the germanium atom's substitution location, the concentration of germanium atoms, and the cross-sectional area of nanowire.

1.2.2 Electron transport

For electron transport, the semi-classical approach (Boltzman's equation) and quantum approach (non-equilibrium Green's function method) are reviewed in section 2.2. In TE device, electron transport determines three important physical quantities: the Seebeck coefficient, the electrical conductance and the electron's thermal conductance. After revisiting the physics of TE effect (in section 6.1), it is found the electron's TE efficiency is important and is purely determined by the transmission function of electron transport. A simulation of the TE effect in silicon nanowire is used to demonstrate this concept. Besides that, the effect of electron scattering in TE device is studied by employing non-equilibrium Green's function with Büttiker Probes (in section 6.2). With the understanding of electron transport and its role in TE effect, we propose a TE device with potential high TE efficiency (in section 6.3).

CHAPTER II

LITERATURE REVIEW

2.1 Phonon Transport

In this section, the background of phonon transport is given. The thermal energy and the specific heat capacity problem are introduced in the section 2.1.1. In the section 2.1.2, the concept of phonon is illustrated by using harmonic oscillator as an example. Then, dynamical matrix is introduced to model the lattice vibration (section 2.1.3). In the last (section 2.1.4), a unified model of phonon transport and the basic formula of this model are given.

2.1.1 Thermal Energy

Temperature T is the most important dynamical variable to describe the thermal energy of a system. When a system is in thermal equilibrium, the temperature of the system is well defined. The temperature is proportional to the mean energy of particles in the system[26]. In this case, the temperature is recognized as a macroscopic parameter to describe thermal energy of the system.

In our work, the system we are interested in is solid, especially crystalline solid. If the temperature of a crystal increases, its thermal energy increases as well. The relation between the change in thermal energy ΔE and the change in temperature ΔT is given by the equation:

$$\Delta E = C \Delta T, \tag{1}$$

where C stands for the specific heat capacity. Specific heat capacity is firstly recognized as an intrinsic property of the crystal itself, and has been the subject of study for quite a long time. In 19th century, the law of Dulong-Petit was established[27, 28]:

Thermal energy is the manifestation of the vibration of atoms in crystal. Each atom has 6 degrees of freedom to vibrate, (i.e. 3 in location and 3 in velocities for 3-dimensional system). At temperature T , each degree of freedom has thermal energy $\frac{1}{2}k_B T$, where k_B is Boltzmann constant. Thus, the thermal energy E of a crystal with N atoms is:

$$E = 3Nk_B T. \quad (2)$$

With Eq.(2), the specific heat capacity of the crystal

$$C = \frac{\partial E}{\partial T} = 3Nk_B. \quad (3)$$

From Eq.(3), the specific heat is independent of temperature. The specific heat capacity derived from Dulong-Petit's law works very well in high temperature region (normally referred to room temperature and above), but the law fails when temperature is low, that is the specific heat capacity is decreasing with temperature. To find the physical origin of this problem, the detailed analysis of thermal property in crystal was carried out. The vibration of atoms are modelled by harmonic oscillators and the concept of phonon was introduced. In 1907, Einstein established the Einstein's Model to calculate specific heat capacity. Later, Debye (1912) elaborated on this concept and created Debye's Model. In the same year, Born and von Karman's research contributed significantly to the concept of phonon. These approaches adopted the concept of phonon as a quantized model of lattice vibration.

2.1.2 Phonon

Thermal energy in crystal is carried by the vibration of atoms. With harmonic approximation, this vibration is modelled by harmonic oscillators, in which thermal energy is quantized (the smallest quanta is known as a phonon). To illustrate the concept of phonon [29], a single particle harmonic oscillator is considered and its Hamiltonian in classical mechanics is:

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \quad (4)$$

where x and p are the position and momentum of the particle harmonic oscillator respectively, and ω is the oscillation frequency. Instead of dynamical variable in classical mechanics, position and momentum are represented by operators X and P , which will be acting on the wave function in quantum mechanics:

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2. \quad (5)$$

The Schrödinger equation of the single particle harmonic oscillator is

$$\left(\frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2\right)\psi(x) = E\psi(x), \quad (6)$$

where E is the energy of the harmonic oscillator. To find the solution of Eq.(6), we follow Dirac: the Hamiltonian operator is factorized and expressed by the product of other two operators. With the definition of a , $a^\dagger$ and N as:

$$\begin{aligned} a &= \frac{X}{\sqrt{2\hbar/m\omega}} + \frac{iP}{\sqrt{2m\omega\hbar}}, \\ a^\dagger &= \frac{X}{\sqrt{2\hbar/m\omega}} - \frac{iP}{\sqrt{2m\omega\hbar}}, \\ N &= a^\dagger a, \end{aligned}$$

we have

$$\begin{aligned} N &= \left(\frac{X}{\sqrt{2\hbar/m\omega}} - \frac{iP}{\sqrt{2m\omega\hbar}}\right)\left(\frac{X}{\sqrt{2\hbar/m\omega}} + \frac{iP}{\sqrt{2m\omega\hbar}}\right) \\ &= \frac{1}{\hbar\omega}\left(\frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 + i\frac{[X, P]}{2}\omega\right). \end{aligned}$$

Due to the uncertainty principle, the commutation of position and momentum is:

$$[X, P] = i\hbar. \quad (7)$$

So the Hamiltonian of the single particle harmonic oscillator is

$$H = \hbar\omega\left(N + \frac{1}{2}I\right), \quad (8)$$

where I is the identity matrix. The term " $\frac{1}{2}I$ " is trivial, as it is shifting the eigen value of the system only. The operator N plays an important role in the system, and the operator N can be treated as equivalent to Hamiltonian operator H .

Before solving for operator N , some important properties of operator a and $a^\dagger$ should be mentioned. With uncertainty principle denoted by Eq.(7), the commutation of a and $a^\dagger$ is

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = 1. \quad (9)$$

Let $|\lambda\rangle$ be an eigen vector of operator N with the eigen value λ , so

$$N|\lambda\rangle = \lambda|\lambda\rangle. \quad (10)$$

Also, by using the properties mentioned in Eq.(9),

$$Na|\lambda\rangle = a^\dagger aa|\lambda\rangle = (aa^\dagger - 1)a|\lambda\rangle = (\lambda - 1)a|\lambda\rangle, \quad (11)$$

and

$$Na^\dagger|\lambda\rangle = a^\dagger aa^\dagger|\lambda\rangle = (aa^\dagger + 1)a^\dagger|\lambda\rangle = (\lambda + 1)a^\dagger|\lambda\rangle. \quad (12)$$

Eq.(11) shows that the vector $a|\lambda\rangle$ is an eigen vector of operator N with the eigenvalue $\lambda - 1$. Similarly, Eq.(12) shows that the vector $a^\dagger|\lambda\rangle$ is also an eigen vector of operator N with the eigenvalue $\lambda + 1$. Because operator N is Hermitian, thus the eigen value must be real and positive. Furthermore, due to Eq.(11), the operator a acting on vector $|\lambda\rangle$ decrease the eigen value of N by 1, thus the minimum value of λ equals to 0. Because of Eq.(12), the operator $a^\dagger$ acting on vector $|\lambda\rangle$, increases the eigen value of N by 1, so λ could be equal to any non-negative integers. So for the system which is a harmonic oscillator, the eigen value is

$$E = \hbar\omega(n + \frac{1}{2}), \quad (13)$$

where n is non-negative integer. That means the energy of the system is quantized, the energy between two neighboring states is $\hbar\omega$. The amount of energy $\hbar\omega$ is the

smallest quota that the energy of the system could vary, and that amount of energy is referred as the energy of a phonon with frequency ω . N is number operator telling the number of phonon in the system. a is annihilation operator, which destroy a phonon. $a^\dagger$ is creation operator, which create one phonon in the system. In a crystal, the lattice vibration is treated as many orthogonal harmonic oscillators.

2.1.3 Lattice Vibration

A crystal can be viewed as unit cells being placed into lattice structure. Therefore, the atomic vibration in crystal is related to the vibration property of its lattice. To study lattice vibration, we follow Callaway's book[30]. Let's consider an infinite large crystal, hence the boundary effect is neglected. The i^{th} unit cell of the crystal is represent by a space vector R_i . In i^{th} unit cell, there are r atoms (r is a integer), and the κ^{th} atom's position is denoted by vector $X_{i\kappa}$. With the presence of heat energy ($T \neq 0K$), atoms are vibrating at their equilibrium positions, the displacement of κ^{th} atom in i^{th} unit cell from its equilibrium position is denoted by a vector $u_{i\kappa}$. With M_κ (the mass of κ^{th} atom), the total kinetic energy of the crystal is

$$T = \frac{1}{2} \sum_{\alpha, i, \kappa} M_\kappa (\dot{u}_{\alpha, i\kappa})^2, \quad (14)$$

where $u_{\alpha, i\kappa}$ is α^{th} component of the atom displacement vector $u_{i\kappa}$ (normally, $\alpha = 1, 2, 3$ to represent x,y,z direction), the upper dot means the first derivative with respect to time. Because atoms are bonding to each other in crystal, they experience forces from nearby atoms. The force is expressed as a function of the atomic displacement, so does the potential energy. With harmonic approximation, higher order terms (order greater than 2) in potential energy are neglected, as

$$\Phi = \Phi_0 + \sum_{i\kappa\alpha} \Phi_{\alpha, i\kappa} u_{\alpha, i\kappa} + \frac{1}{2} \sum_{i\kappa\alpha, j\nu\beta} \Phi_{\alpha\beta, i\kappa, j\nu} u_{\alpha, i\kappa} u_{\beta, j\nu}, \quad (15)$$

where Φ_0 is the potential energy when all atoms are at equilibrium position, $\Phi_{\alpha, i\kappa}$ and $\Phi_{\alpha\beta, i\kappa, j\nu}$ are first and second derivatives of the potential energy with respect to

atomic displacement and evaluated at equilibrium position:

$$\begin{aligned}\Phi_{\alpha,i\kappa} &= \left[\frac{\partial \Phi}{\partial u_{\alpha,i\kappa}} \right]_0, \\ \Phi_{\alpha\beta,i\kappa,j\nu} &= \left[\frac{\partial^2 \Phi}{\partial u_{\alpha,i\kappa} \partial u_{\beta,j\nu}} \right]_0.\end{aligned}\tag{16}$$

The equilibrium positions of atoms are at fixed points, when atoms vibrate. So, when an atom at its equilibrium position, the net force acting on the atom is zero, which means $\Phi_{\alpha,i\kappa} = 0$. Thus, first order term in potential energy is removed:

$$\Phi = \Phi_0 + \frac{1}{2} \sum_{i\kappa\alpha,j\nu\beta} \Phi_{\alpha\beta,i\kappa,j\nu} u_{\alpha,i\kappa} u_{\beta,j\nu}.\tag{17}$$

Therefore, the Hamiltonian of the system is

$$H = \Phi_0 + \frac{1}{2} \sum_{i\kappa\alpha} M_k (\dot{u}_{\alpha,i\kappa})^2 + \frac{1}{2} \sum_{i\kappa\alpha,j\nu\beta} \Phi_{\alpha\beta,i\kappa,j\nu} u_{\alpha,i\kappa} u_{\beta,j\nu}.\tag{18}$$

From the Hamiltonian equation denoted by Eq.(18), by assuming the total energy of the crystal is unchanged, the equation of motion for each atom can be derived:

$$M_k \ddot{u}_{\alpha,i\kappa} = - \sum_{j\nu\beta} \Phi_{\alpha\beta,i\kappa,j\nu} u_{\beta,j\nu}.\tag{19}$$

When an atom vibrates, the format of the vibration is propagating to other nearby atoms through the coupling strength. Due to the periodicity of the lattice, the atom's displacement (or vibration) has a wave-like periodic solution to the equation of motion (indicated by Eq.(19)),

$$u_{\alpha,i\kappa} = M_\kappa^{-1/2} u_{\alpha,\kappa}(k) \exp[-i\omega t + ik \cdot R_i],\tag{20}$$

where k is the wave vector indicating the propagation direction. By substituting the periodic solution (Eq.(20)) back to the equation of motion (Eq.(19)), we have

$$\begin{aligned}& -M_\kappa^{-1/2} \omega^2 \exp[-i\omega t + ik \cdot R_i] u_{\alpha,\kappa}(k) \\ &= - \sum_{j\nu\beta} M_\nu^{-1/2} \Phi_{\alpha\beta,i\kappa,j\nu} u_{\alpha,\kappa}(k) \exp[-i\omega t + ik \cdot R_i + ik \cdot (R_j - R_i)].\end{aligned}\tag{21}$$

Because Φ depends only on $R_i - R_j$, we then have the set of simultaneous equations

$$\omega^2 u_{\alpha,\kappa}(k) = \sum_{\nu\beta} D_{\alpha\beta,\kappa\nu}(k) u_{\beta,\nu}(k), \quad (22)$$

where

$$D_{\alpha\beta,\kappa\nu}(k) = (M_\kappa M_\nu)^{-1/2} \sum_{R_i - R_j} \Phi_{\alpha\beta,i\kappa,j\nu} \exp[ik \cdot (R_j - R_i)]. \quad (23)$$

Here D is dynamical matrix and ω is the vibration frequency. By combining the set of simultaneous equations in a matrix form, we have

$$\omega^2 u(k) = D(k)u(k), \quad (24)$$

where D is $3r \times 3r$ square matrix and r stands for the number of atoms in the system, $u(k)$ is a vector constructed by atomic displacement of each atom.

The set of linear equations (Eq.(24)) will have non trivial solution when

$$[\omega^2 I - D(k)]u(k) = 0.$$

Thus, it turns out to be an eigen value problem. The eigen values of dynamical matrix D are the solutions for ω^2 , where the corresponding eigen vectors are solutions for $u(k)$. The eigen vectors tells the direction of atomic vibration at that particular frequency ω . For a given wave vector k , there are $3r$ set of eigen values and eigen vectors, each set is named as a vibration mode. Each mode can be viewed as a harmonic oscillator with the vibration frequency ω .

2.1.4 Phonon Transport

To study phonon transport, a two-probe system is normally considered. The two probes served as thermal contacts, where one contact has higher temperature than the other, and the thermal energy flows from the contact with a higher temperature to a lower one. The amount of heat energy flowing in unit time is known as thermal current I_Q , and it is determined by

$$I_Q = -K\Delta T, \quad (25)$$

where K is thermal conductance by phonon and ΔT is the temperature difference between the two contacts. In bulk case, thermal conductance can be determined from the conductivity with the system's geometrical parameters. However, this relation may not be true, when the structure goes to nano-meter scale. The major reason is the boundary effect and the large surface to volume ratio, which significantly affect the thermal conductance. Furthermore, the contact interface between the nano-structure and contacts becomes important. This is because the termination of the periodic lattice structure at the contact interface results in phonon scattering and reflection.

The contact interface problem was firstly addressed by acoustic match method, the transmission and reflection coefficients could be determined by the model. But, the transmission and reflection are not energy dependent, which is not generally true to address the phonon transport at the contact interface. This is because phonons have their own direction and energy, indexed by wave vector k and frequency ω respectively. When phonons go through the contact interface, phonon scattering and reflection are different for each phonon mode. Thus, the transmission probability of each phonon modes need to be carefully considered. With the transmission probability of each phonon mode, the conductance of the system is determined. However, the process of calculating transmission for each mode is a very tedious one.

Computational methods are important tools in the investigation of phonon transport. At first, molecular dynamics is used. In molecular dynamics, each atom is treated as a classical particle and obeys Newton's law. The force acting on atom is usually determined from the force field modeled by an empirical potential. With fixed environmental parameter (i.e. volume, temperature, and pressure), acceleration, velocity and position of each atom are monitored for a certain period. By analyzing the atoms' information in that period statistically, the thermal conductance by phonon of the system is determined. In the past twenty years, molecular dynamics method gives a very good explanation and verification on phonon transport theory, especially

Figure 1: Modeled system of phonon transport, a two-probe system.

in the high temperature region. However, molecular dynamics is based on classical mechanics, and it does not work in the low temperature region.

In recent years, quantum phenomena was adopted in the computation of phonon transport[31]. With the development of the non-equilibrium Green's function in phonon transport [32, 33, 34], which is based on quantum mechanics, phonon transport can be analyzed effectively and systematically. In the following, we are going to introduce the unified model, a two-probe system with non-equilibrium Green's function, which is used in our research project.

The two-probe system is shown in Fig.1. A wire (which can be a nano-wire or atomic wire,) is coupled by two thermal contacts. The temperature of the left contact is higher than the right one, i.e. $T_l > T_r$. With the assumption that thermal equilibrium is in the two thermal contacts, according to the Bose-Einstein distribution, number of phonons on a state is known. If the phonon density of states of two thermal contacts are identical, more phonons are in the higher temperature thermal contact

(shown in Fig.1), that results in phonon flow.

The phonon transport properties depends on two physical quantities in the system. One is the phonon density of state in the wire, which is determined by the dynamical matrix D . The other is the self-energy Σ , which describes the couplings between wire and contacts. When phonons go into the wire from thermal contact, there are two issues to be addressed. The first issue is "Is it possible to go into the wire?". If the wire does not have the phonon mode of a phonon, such phonon has to be scattered to a phonon mode in wire before going through the interface, or such phonon is reflected back to the thermal contact. The other issue is "how easy is it for a phonon to go through the interface?". That is described by the bonding between thermal contacts and the wire. When isolating the wire from the contacts, the effect of the bonding is modeled by the self-energy of the wire.

When using non-equilibrium Green's function method to investigate the phonon transport of the system, the central wire is singled out for analysis. The dynamical matrix of the central wire D is constructed by the inter-atomic elastic constant. Self-energies of the left and right thermal contact, Σ_L and Σ_R , describes the coupling between wire and thermal contacts. Then, the retarded Green's function of the wire G^R is given as:[35]

$$G^R(\omega) = [(\omega + i\delta)^2 + D - \Sigma]^{-1}, \quad (26)$$

where ω is phonon frequency and δ is approaching 0^+ . The phonon density of state can be expressed in terms which are determined by the retarded Green's Function, as the following equation:

$$DOS_{phonon} = -\frac{\text{Im}[G^R(\omega)]}{\pi}. \quad (27)$$

Other types of Green's function can be expressed in terms of the retarded Green's function. For example, the advanced Green's function is given by:

$$G^A(\omega) = G^R(\omega)^\dagger. \quad (28)$$

Also, the lesser and greater Green's Function, $G^<$ and $G^>$, is found in Eqs.(29 and 30), in which $\Sigma^<$ and $\Sigma^>$ are lesser and greater self-energies.

$$G^>(\omega) = G^R(\omega)\Sigma^>(\omega)G^A(\omega) \quad (29)$$

$$G^<(\omega) = G^R(\omega)\Sigma^<(\omega)G^A(\omega) \quad (30)$$

The lesser and greater self-energies are determined in following way:

$$\Sigma^>(\omega) = -i \cdot [n(\omega, T) + 1] \cdot \Gamma, \quad (31)$$

$$\Sigma^<(\omega) = -i \cdot n(\omega, T) \cdot \Gamma,$$

where the broadening function Γ is given by

$$\Gamma = -2 \text{Im}[\Sigma^R(\omega)],$$

and the Bose-Einstein distribution $n(\omega, T)$ is

$$n(\omega, T) = [1 - e^{\frac{\hbar\omega}{k_B T}}]^{-1}.$$

Finally, the thermal current by phonon is expressed in the form of non-equilibrium Green's Function and self-energies:

$$I = -\frac{\hbar}{4\pi} \int d\omega \cdot \omega \cdot \text{Tr}[\Sigma^<(\omega) \cdot G^>(\omega) - \Sigma^>(\omega) \cdot G^<(\omega)]. \quad (32)$$

2.2 Electron Transport

In this section, the two methods of electron transport are reviewed. The first method is the semi-classical approach, using Boltzmann's equation with relaxation time approximation (section 2.2.1). In this method, the electron distribution function plays an important role in determining the charge current and thermal current by electron. The second method is Non-equilibrium Green's function method [35] (section 2.2.2), which is a quantum mechanical approach. Generally, the current determined by this method is ballistic. To consider scattering effect, Büttiker probe is introduced.

2.2.1 Semi-classical approach

2.2.1.1 Boltzmann's equation

Boltzmann equation is a semi-classical approach to determining the transport properties [36]. Let $f(k, r, t)$ be the probability of electron occupation at the state with wave vector k , position r and time t . Due to the force F_t , electrons are changing their positions and wave vectors. Generally, the force F_t is including the applied force F and the force F_c due to electron collisions with lattice vibrations and other imperfections in the crystal, but not the periodic crystal forces. Hence, the probability of electron occupation at the state with vector $k + dk$, position $r + dr$ and time $t + dt$ is given by

$$f(k + dk, r + dr, t + dt) = f(k + \frac{1}{\hbar}F_t dt, r + v dt, t + dt). \quad (33)$$

Also, the rate of change in the distribution function is

$$\frac{df}{dt} = \frac{1}{\hbar}F_t \cdot \nabla_k f + v \cdot \nabla_r f + \frac{\partial f}{\partial t}. \quad (34)$$

On the right side of the equation, the term $(\frac{1}{\hbar}F_t \cdot \nabla_k f)$ is due to the force F_t , the term $(v \cdot \nabla_r f)$ accounts for the concentration gradients, and the last term $(\frac{\partial f}{\partial t})$ is for the local change at position r . The Eq.(34) is regarded as Boltzmann's transport equation.

At a steady condition, the force F_t is unchanged and number of states in crystal is a constant, the rate of change of the distribution function must be zero (Liouville's theorem), hence

$$\frac{\partial f}{\partial t} = -\frac{1}{\hbar}F_t \cdot \nabla_k f - v \cdot \nabla_r f. \quad (35)$$

Because of the difficulty in determining the force F_c , which induces electron scattering, relaxation time approximation is normally adopted to model the local change of the distribution:

$$\frac{\partial f}{\partial t} = \frac{-(f - f_0)}{\tau_m}, \quad (36)$$

where f_0 is the equilibrium distribution function and τ_m the relaxation time. From Eq.(35 and 36), the steady-state Boltzmann equation with the relaxation time approximation is

$$f = f_0 - \frac{\tau_m}{\hbar} F_t \cdot \nabla_k f - \tau_m v \cdot \nabla_r f. \quad (37)$$

By using the relation

$$\nabla_k f = \frac{\partial f}{\partial E} \nabla_k E \quad (38)$$

and

$$v = \frac{1}{\hbar} \nabla_k E, \quad (39)$$

Eq.(37) becomes

$$f = f_0 - \frac{\tau_m}{\hbar} v \left(\frac{\partial f}{\partial E} F + \nabla_r f \right). \quad (40)$$

The Boltzmann equation in the form of Eq.(40) tells us that the non-equilibrium distribution of electrons depends on the scattering processes through the relaxation time τ_m , on the band structure through $\nabla_k E$, on applied forces through $\frac{\partial f}{\partial E} F$, on concentration gradients through $\nabla_r f$. Hence, To determine the non-equilibrium distribution function is a process of solving the partial differential equation.

2.2.1.2 Electrical conductivity

In this section, a three dimensional bulk material is considered. The electrical conductivity is evaluated with a static electric field E_{dc} and uniform temperature[37]. The electron distribution function for wave vector k is given by:

$$f(k) = f_0(k) - e E_{dc} v(k) \tau(E(k)) \left(-\frac{\partial f}{\partial E} \right), \quad (41)$$

where e is unit of charge. Since the number of electrons per unit volume in the volume element dk is $f(k)dk/(4\pi^3)$, the current density in a electron band n is

$$j^n = -e \int \frac{dk}{4\pi^3} v(k) g(k).$$

For fully filled electron band, current density is 0. This is because an electron with wave vector $-k$ counterbalance the contribution of the electron with wave vector k to current density. Therefore, the total current density is the sum of the contributions from each partially filled band. With the definition of electrical conductivity

$$\sigma = \sum_n \frac{j^n}{E_{dc}} = \sum_n \sigma^n, \quad (42)$$

the electrical conductivity for band n is

$$\sigma^n = e^2 \int \frac{dk}{4\pi^3} \tau_n(E_n(k)) v_n^2(E(k)) \left(-\frac{\partial f}{\partial E}\right). \quad (43)$$

2.2.1.3 Thermal conductivity

To determine the thermal conductivity, a uniform static electric field and temperature gradient is considered[37]. Hence, the electron distribution is

$$f(k) = f_0(k) + \tau(E(k)) \left(-\frac{\partial f}{\partial E}\right) v(k) \cdot \left[-eE_{dc} + \frac{E(k) - \mu}{T} (-\nabla T)\right], \quad (44)$$

The thermal current density j^q is proportional to the entropy current density j^s of the electrons, which intimately relates to the internal energy and number of electrons, as:

$$j^q = T \cdot j^s = j^\varepsilon - \mu j^n. \quad (45)$$

In above equation, j^ε and j^n are the energy and number current densities, and they are given by

$$j^\varepsilon = \sum_n \int \frac{dk}{4\pi^3} E_n(k) v_n(k) f_n(k), \quad (46)$$

and

$$j^n = \sum_n \int \frac{dk}{4\pi^3} v_n(k) f_n(k). \quad (47)$$

By substituting Eqs.(46 and 47) into Eq.(45), the thermal current density is

$$j^q = \sum_n \int \frac{dk}{4\pi^3} [E_n(k) - \mu] v_n(k) f_n(k). \quad (48)$$

From the distribution function indicated by Eq.(44), the electrical current and thermal current can be expressed in the form:

$$\begin{aligned} j &= L^{11}E_{dc} + L^{12}(-\nabla T), \\ j^q &= L^{21}E_{dc} + L^{22}(-\nabla T), \end{aligned} \quad (49)$$

where the matrices L^{ij} are defined in terms of

$$X^{(a)} = e^2 \int \frac{dk}{4\pi^3} \left(-\frac{\partial f}{\partial E}\right) \tau(k) v^2(k) (E(k) - \mu)^a \quad (50)$$

by

$$\begin{aligned} L^{11} &= X^{(0)}, \\ L^{21} &= T \cdot L^{12} = -\frac{1}{e} X^{(1)}, \\ L^{22} &= \frac{1}{e^2 T} X^{(2)}. \end{aligned} \quad (51)$$

The thermal conductivity is evaluated in the condition of a temperature gradient without electric current flows ($j = 0$), and is defined as:

$$\kappa = \frac{j^q}{(-\nabla T)}. \quad (52)$$

Thus, from Eq.(49), the thermal conductivity is given by

$$\kappa = L^{22} - L^{21}(L^{11})^{-1}L^{12}. \quad (53)$$

To set the electric current to zero, an electrical potential is produced by the temperature gradient. From Eq.(49), the Seebeck coefficient, defined as the proportionality constant between the voltage produced and the temperature difference, is given by:

$$S = \frac{L^{12}}{L^{11}}. \quad (54)$$

2.2.2 Non-equilibrium Green's Function Method

2.2.2.1 Green's function

The Schrödinger equation of a device with two contacts is

$$H |\psi\rangle = E |\psi\rangle ,$$

and can be discretized into the follow form[38]:

$$\begin{pmatrix} H_1 & \tau_1 & 0 \\ \tau_1^\dagger & H_d & \tau_2^\dagger \\ 0 & \tau_2 & H_2 \end{pmatrix} \begin{pmatrix} |\psi_1\rangle \\ |\psi_d\rangle \\ |\psi_2\rangle \end{pmatrix} = E \begin{pmatrix} |\psi_1\rangle \\ |\psi_d\rangle \\ |\psi_2\rangle \end{pmatrix} , \quad (55)$$

where H_1 , H_2 and H_d are the Hamiltonian of the contacts 1 and 2 and the device, τ_1 and τ_2 are the coupling matrix between contacts and device. Green's Function is defined as:

$$(E - H)G(E) = I. \quad (56)$$

When there is a constant perturbation $|v\rangle$, the Schrödinger equation becomes:

$$H |\psi\rangle = E |\psi\rangle + |v\rangle , \quad (57)$$

and it can be rewritten into:

$$|\psi\rangle = -G(E) |v\rangle . \quad (58)$$

That means the Green's function is actually the response of a system to a constant perturbation. Instead of solving Schrödinger equation, (a whole eigenvalue problem,) Green's function provides an easier method to investigate the system. For example, the wave function of the contact ($|\psi_2\rangle$) can be calculated from the third row of Eq.(55), if the wave function of the device ($|\psi_d\rangle$) is known:

$$\tau_2 |\psi_d\rangle + H_2 |\psi_2\rangle = E |\psi_2\rangle \quad (59)$$

$$(E - H_2) |\psi_2\rangle = \tau_2 |\psi_d\rangle \quad (60)$$

$$|\psi_2\rangle = G_2(E) \tau_2 |\psi_d\rangle , \quad (61)$$

where $G_2(E)$ is the Green's function of the isolated contact 2, i.e.

$$(E - H_2)G_2(E) = I. \quad (62)$$

There are two types of solutions for the Green's function, the retarded Green's function G and the advanced Green's function $G^\dagger$, which correspond to the outgoing and incoming waves in the contacts.

2.2.2.2 Self-Energy

It is important to note that the system we discussed previously is infinite. With Self-Energy employed, the system can be divided into small parts, that reduce the complexity to solve the problem. That means, we are not going to solve the Green's function for the whole system, but the Green's function for the parts we are interested in.

With the definition of Green's function, the matrix form of Eq.(56) is:

$$\begin{pmatrix} E - H_1 & -\tau_1 & 0 \\ -\tau_1^\dagger & E - H_d & -\tau_2^\dagger \\ 0 & -\tau_2 & E - H_2 \end{pmatrix} \begin{pmatrix} G_1 & G_{1d} & G_{12} \\ G_{d1} & G_d & G_{d2} \\ G_{21} & G_{2d} & G_2 \end{pmatrix} = \begin{pmatrix} I & 0 & 0 \\ 0 & I & 0 \\ 0 & 0 & I \end{pmatrix}. \quad (63)$$

Since, we are only interested in the device, the equations related to G_d are

$$(E - H_1)G_{1d} - \tau_1 G_d = 0, \quad (64)$$

$$-\tau_1^\dagger G_{1d} + (E - H_d)G_d - \tau_2^\dagger G_{2d} = I, \quad (65)$$

$$-\tau_2 G_d + (E - H_2)G_{2d} = 0. \quad (66)$$

The Green functions G_{1d} and G_{2d} can be solved from Eqs.(64 and 66),

$$G_{1d} = G_1 \tau_1 G_d, \quad (67)$$

$$G_{2d} = G_2 \tau_2 G_d, \quad (68)$$

the solutions are substituted into Eq.(65) to give:

$$-\tau_1^\dagger G_1 \tau_1 G_d + (E - H_d)G_d - \tau_2^\dagger G_2 \tau_2 G_d = I. \quad (69)$$

With Self-Energies of the device to the contacts defined as:

$$\Sigma_1 = \tau_1^\dagger G_1 \tau_1 \quad (70)$$

$$\Sigma_2 = \tau_2^\dagger G_2 \tau_2, \quad (71)$$

Eq.(69) is rearranged into the form:

$$G_d = (E - H_d - \Sigma_1 - \Sigma_2)^{-1}. \quad (72)$$

2.2.2.3 The spectral function

Assume, a constant perturbation $|v\rangle$ is in the system, the two Green's functions are the solutions of Eq.(58), which can be expressed as:

$$|\psi\rangle^R = -G |v\rangle, \quad (73)$$

$$|\psi\rangle^A = -G^\dagger |v\rangle. \quad (74)$$

The spectral function A is defined as the difference between retarded and advanced Green's function,

$$A = i(G - G^\dagger),$$

and the product of the spectral function to any vector $|v\rangle$ is a solution to the Schrödinger equation:

$$\begin{aligned} (E - H)A |v\rangle &= (E - H)i(G - G^\dagger) |v\rangle \\ &= i(I - I) |v\rangle = 0. \end{aligned}$$

Also, The spectral function gives the electron density of states. To show that, Green's function are written in the form of eigen basis:

$$G = (E + i\delta - H)^{-1} = \sum_k \frac{|k\rangle \langle k|}{E + i\delta - E_k}, \quad (75)$$

$$G^\dagger = (E - i\delta - H)^{-1} = \sum_k \frac{|k\rangle \langle k|}{E - i\delta - E_k}, \quad (76)$$

where δ is an infinitesimal number. With that, the spectral function is

$$A(E) = \sum_k |k\rangle \langle k| \frac{2\delta}{(E - E_k)^2 + \delta^2}. \quad (77)$$

When δ goes to zero, we obtain

$$A(E) = 2\pi \sum_k \delta(E - E_k) |k\rangle \langle k|, \quad (78)$$

where $\delta(E - E_k)$ is the delta function. Eq.(78) shows that the spectral function gives all solutions to the Schrödinger equation and gives the density of states.

2.2.2.4 Electrical Current

In steady state, the number of electrons in the device is conserved, which means the rate of change in number of electron equals to zero, i.e.

$$\frac{\partial \sum_i |\psi_i|^2}{\partial t} = 0. \quad (79)$$

The left term of the above equation can be rearranged as:

$$\begin{aligned} \frac{\partial \sum_i |\psi_i|^2}{\partial t} &= \sum_i \frac{\partial \langle \psi | i \rangle \langle i | \psi \rangle}{\partial t} = \sum_i \left(\frac{\partial \langle \psi | i \rangle}{\partial t} \langle i | \psi \rangle + \langle \psi | i \rangle \frac{\partial \langle i | \psi \rangle}{\partial t} \right) \\ &= \frac{i}{\hbar} \sum_i (\langle \psi | H | i \rangle \langle i | \psi \rangle - \langle \psi | i \rangle \langle i | H | \psi \rangle) \\ &= \frac{i}{\hbar} (\langle \psi | H | \psi_d \rangle - \langle \psi_d | H | \psi \rangle) \\ &= \frac{i}{\hbar} (\langle \psi | H_d + \tau_1 + \tau_2 | \psi_d \rangle - \langle \psi_d | H + \tau_1^\dagger + \tau_2^\dagger | \psi \rangle) \\ &= \frac{i}{\hbar} ([\langle \psi_1 | \tau_1 | \psi_d \rangle - \langle \psi_d | \tau_1^\dagger | \psi_1 \rangle] - [\langle \psi_2 | \tau_2 | \psi_d \rangle - \langle \psi_d | \tau_2^\dagger | \psi_2 \rangle]). \end{aligned} \quad (80)$$

The first square bracket is interpreted as the incoming probability current into the device from contact 1, while the second bracket is from contact 2. Thus, for contact j , the electrical current is the product of the probability current times the charge of electron, that gives

$$i_j = -\frac{i \cdot e}{\hbar} (\langle \psi_j | \tau_j | \psi_d \rangle - \langle \psi_d | \tau_j^\dagger | \psi_j \rangle). \quad (81)$$

When reservoirs are with different chemical potential, electrons will be injected to occupy the states corresponding to incoming waves in the contacts. Assume the incoming wave has the wave function $|\psi_{1,n}\rangle$ in isolated contact 1, the wave function for the whole system is then $|\psi_{1,n}\rangle + |\psi^R\rangle$, and the Schrödinger equation become:

$$\begin{pmatrix} H_1 + \tau_1 + \\ H_d + \tau_1^\dagger + \tau_2^\dagger \\ H_2 + \tau_2 \end{pmatrix} (|\psi_{1,n}\rangle + |\psi^R\rangle) = E(|\psi_{1,n}\rangle + |\psi^R\rangle)$$

$$\begin{aligned} E|\psi_{1,n}\rangle + \tau_1^\dagger|\psi_{1,n}\rangle + H|\psi^R\rangle &= E(|\psi_{1,n}\rangle + |\psi^R\rangle) \\ H|\psi^R\rangle &= E|\psi^R\rangle - \tau_1^\dagger|\psi_{1,n}\rangle. \end{aligned} \quad (82)$$

Hence, the perturbation is $-\tau_1^\dagger|\psi_{1,n}\rangle$. From Eq.(58), we obtained:

$$|\psi^R\rangle = G\tau_1^\dagger|\psi_{1,n}\rangle. \quad (83)$$

Also, the wave function of the device can be express in terms of its Green's function and the incoming wave function, as:

$$|\psi_d\rangle = G_d\tau_1^\dagger|\psi_{1,n}\rangle. \quad (84)$$

From Eq.(61), the wave function of contact 2 is:

$$|\psi_2\rangle = G_2\tau_2|\psi_d\rangle = G_2\tau_2G_d\tau_1^\dagger|\psi_{1,n}\rangle. \quad (85)$$

For the wave function in contact 1, it is similar to contact 2, but the incoming wave function should be added, that is:

$$|\psi_1\rangle = G_1\tau_1G_d\tau_1^\dagger|\psi_{1,n}\rangle + |\psi_{1,n}\rangle = (1 + G_1\tau_1G_d\tau_1^\dagger)|\psi_{1,n}\rangle. \quad (86)$$

With Eqs.(84, 85 and 86), the current into the device from a incoming wave of

energy E in contact 1 through the coupling τ_2 is:

$$\begin{aligned}
 i_2 &= -\frac{i \cdot e}{\hbar} (\langle \psi_2 | \tau_2 | \psi_d \rangle - \langle \psi_d | \tau_2^\dagger | \psi_2 \rangle) \\
 &= -\frac{i \cdot e}{\hbar} (\langle \psi_{1,n} | \tau_1 G_d^\dagger \tau_2^\dagger G_2^\dagger \tau_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle - \langle \psi_{1,n} | \tau_1 G_d^\dagger \tau_2^\dagger G_2^\dagger \tau_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle) \\
 &= -\frac{i \cdot e}{\hbar} \langle \psi_{1,n} | \tau_1 G_d^\dagger \tau_2^\dagger (G_2^\dagger - G_2) \tau_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle \\
 &= \frac{e}{\hbar} \langle \psi_{1,n} | \tau_1 G_d^\dagger \Gamma_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle,
 \end{aligned}$$

where Γ_2 is the broadening function defined as

$$\Gamma_j = -i(\tau_j^\dagger A_j \tau_j).$$

The total current is

$$\begin{aligned}
 I &= \frac{2e}{\hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] \sum_n \delta(E - E_n) \langle \psi_{1,n} | \tau_1 G_d^\dagger \Gamma_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle \\
 &= \frac{2e}{\hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] \sum_{m,n} \delta(E - E_n) \langle \psi_{1,n} | \tau_1 | m \rangle \langle m | G_d^\dagger \Gamma_2 G_d \tau_1^\dagger | \psi_{1,n} \rangle \\
 &= \frac{2e}{\hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] \sum_m \langle m | G_d^\dagger \Gamma_2 G_d \tau_1^\dagger \left(\sum_n \delta(E - E_n) | \psi_{1,n} \rangle \langle \psi_{1,n} | \right) \tau_1 | m \rangle \\
 &= \frac{2e}{\hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] \sum_m \langle m | G_d^\dagger \Gamma_2 G_d \tau_1^\dagger \frac{A_1}{2\pi} \tau_1 | m \rangle \\
 &= \frac{e}{\pi \hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] \sum_m \langle m | G_d^\dagger \Gamma_2 G_d \Gamma_1 | m \rangle \\
 &= \frac{e}{\pi \hbar} \int dE [f(E, \mu_1) - f(E, \mu_2)] Tr \left(G_d^\dagger \Gamma_2 G_d \Gamma_1 \right).
 \end{aligned}$$

2.2.2.5 Büttiker Probe

In the above current formalism by Non-equilibrium Green's function, the electron transport is purely ballistic in the device. Electron scattering is occurring at the contact surface, only. In order to consider electron scattering effect in the device, Büttiker Probes are introduced[39]. Büttiker Probes are virtual contacts to the device. Electrons flow between the probes and device, but there is no net electron flow, as the probes are virtual. Hence, in the device, the profile of electron occupation in electron states is changed, which is the effect of scattering.

The coupling strength to the device is the only parameter in Büttiker Probe, which is denoted by the self-energy of the probe. The self-energy is determined by the mean free path of electron's in the device. To find out the relation, we consider a device with length L , and the device is discretized by a . That means the spacing between adjacent probes is a . If the net transmission from left to right contacts is T_n , we have the equation

$$\frac{1 - T_n}{T_n} = \frac{L}{a} \cdot \frac{1 - T_p}{T_p}, \quad (87)$$

where the transmission through a single probe T_p is related to the transmission into the probe T_p^{in} by

$$T_p = 1 - \frac{T_p^{in}}{2}. \quad (88)$$

Hence, we obtained

$$\frac{1}{T_n} = 1 + \frac{L}{a} \cdot \frac{T_p^{in}/2}{1 - T_p^{in}/2}. \quad (89)$$

Moreover, the net transmission can be expressed in terms of mean free path λ ,

$$\frac{1}{T_n} = 1 + \frac{L}{\lambda}. \quad (90)$$

In the weak scattering limit, with the relations

$$T_p^{in} = \frac{U_p^2}{t_x^2}, \quad t_x = \frac{\hbar^2}{2m_x^* a^2},$$

where m_x^* is the electron effective mass in x direction, the mean free path is expressed in terms of the coupling strength of Büttiker probe:

$$\lambda = 2a \frac{t_x^2}{U_p^2}. \quad (91)$$

Then, the self-energy of the probe is

$$\Sigma = -\frac{U_p^2}{t_x} e^{ik_x a} = -\frac{2a}{\lambda} t_x e^{ik_x a}. \quad (92)$$

The fermi-level of each probe is adjusted, so that the net electrical current of each probe is zero.

CHAPTER III

EFFECT OF SURFACE BOND RECONSTRUCTION ON THE CONTACTS: PHONON TRANSPORT IN SILICON ATOMIC WIRE

In this chapter[20, 21], the phonon transport properties in a silicon atomic wire coupled to two semi-infinite contacts, is investigated. Moreover, two effects on phonon transport are considered: one is the surface bond reconstruction (SBR) in thermal contacts, the other is the anharmonic effect in atomic wire.

For the demonstration of SBR effect, we use the well known semiconductor material Si for the thermal contacts. Because the contact is semi-infinite, the crystal structure terminates at the contact surface. On the surface layer or a few layers below the surface, atoms experience dissimilar atomic force, which results in reconstruction. The bond length and bond strength are changed, hence the inter-atomic potential. That leads to significant variation in phonon density of state, which further influence the thermal conductance.

The anharmonic effect is the phonon-phonon scattering due to higher order terms in the atomic potential. In most of the cases, this effect is ignored, and phonon transport is considered in a ballistic way. That leads to serious inaccuracy in phonon transport property characterization and thermal conductance calculations in high temperature region.

In order to take these two effects into consideration, the unified model discussed

in chapter 2 is updated and discussed in section 3.1. With this model, results are discussed in section 3.2.

3.1 Theory

3.1.1 Modeled System Description

The modeled system, an atomic wire sandwiched by two thermal contacts, is shown in Fig.2. The atomic wire consists a few silicon atoms connecting in line. For demonstration purpose, two silicon atoms are assumed in the atomic wire. Both thermal contacts are made of silicon crystal, which has face centered cubic (fcc) structure. Each thermal contact is terminated at the contact surface on one end, while there is no termination on the other end. Thus, thermal contacts are semi-infinite. Moreover, on the plane parallel to the contact surface, the crystal has infinite growth. In this system, we set the contact surface of both thermal contacts to be the $(0, 0, 1)$ face of silicon. The coupling strength between two silicon atoms in the atomic wire is t_m , which is known as the stiffness of the atomic wire. Also, the coupling strength between wire and contacts is denoted by t_l and t_r for the left and right thermal contact.

When considering phonon transport in this system, the two thermal contacts are assumed in thermal equilibrium with fixed different temperatures. The temperature of the left thermal contact is denoted by T_l , and T_r is for the right one. Let T_l being greater than T_r , heat is then flowing in the direction from left thermal contact through the wire to the right thermal contact. In this process, a temperature gradient in the thermal contact around the contact surface is expected. Thus, the regions near the coupling point between atomic wire and thermal contact are not in thermal equilibrium, which means the regions are not at the fixed temperature defined previously. To take into account this effect, the region in the contact and near the coupling point between the wire and contact, is treated as a part of the atomic wire[32]. The remaining part of the thermal contact is then assumed to be in thermal equilibrium at fixed

Figure 2: Modeled System: An atomic wire coupled by two semi-infinite silicon thermal contacts.

temperature. The region in left contact is denoted by LD, and RD for the right contact, as shown in Fig.2. The regions LD and RD are set equal to a unit cube of silicon crystal. The original atomic wire D together with the regions LD and RD are treated as a whole wire W, shown in Fig.3, being coupled to the two thermal contacts. By taking out LD and RD regions from the thermal contacts, these regions are treated in non-equilibrium. The whole wire is then modeled using the non-equilibrium Green's functions, hence the non-equilibrium thermal properties of the whole wire W, such as the local heat current and phonon number are determined.

3.1.2 Lennard-Jones potential with SBR effect

Before constructing the dynamical matrix, we need to model the potential energy of the system. Here, we use the famous Lennard-Jones potential for the two body interaction. This is because Lennard-Jones potential is very commonly use in describing a silicon based structure. The original 12-6 Lennard-Jones potential is:

Figure 3: Whole Atomic Wire: The whole atomic wire, LD and RD regions are set to be one unit cell of silicon crystal.

$$V = 4\varepsilon_0\left[\left(\frac{\sigma}{d}\right)^{12} - \left(\frac{\sigma}{d}\right)^6\right], \quad (93)$$

where ε_0 is the depth of the potential well, σ is the distance at which the interparticle potential is zero, and d is the distance between the particles.

Due to the termination of crystal structure at the contact surface, surface bond reconstruction (SBR) occurs and affects the phonon transport in atomic wire. On the surface and a few layers below it, both the bond strength and inter-atomic distances are very different from the bulk case. This causes the inter-atomic potentials and hence the inter-atomic elastic constants around the contact surface to differ from those deep inside the contacts. The modifications of the inter-atomic elastic constants around the contact surfaces would change the phonon surface density of states of the contacts and affect the scattering of various incident phonons propagating through the wire. It is then expected that SBR near the contact surfaces would modify the thermal conductance of the atomic wire, which is coupled to the thermal contact surface.

In principle, we need to first find the SBR for Si and then determine the modification of the inter-atomic elastic constants near the contact surface. Due to the complexity and difficulty of obtaining the accurate calculation of SBR near a Si surface, we instead use a simplified theoretical model for SBR near a Si surface. According to Sun's work[40], SBR only occurs in the first three layers of atoms (denoted by $i = 1, 2, 3$) near the surface. The averaged bond contraction coefficient between the layer i and the layer $i + 1$ of atoms is given by

$$\frac{d_i}{d_0} = \frac{2}{1 + e^{[(z_0 - z_i)/8z_i]}}, \quad (i = 1, 2), \quad (94)$$

where d_0 and z_0 denote bond length between neighboring layers and atomic coordination number in the bulk, respectively. And z_i ($i = 1, 2$), is the atomic coordination number for the atoms in the first and the second layer. Furthermore, the modified bond energy ε_i (due to bond contraction) between the layer i and layer $i + 1$ is given by

$$\varepsilon_i = \varepsilon_0 \cdot \left(\frac{d_i}{d_0}\right)^{-m}, \quad (95)$$

where ε_0 denotes the bond energy in the bulk. Sun[41] proposed that for Si, $z_1 = 4$, $z_2 = 6$, $z_0 = 12$ and $m = 4.88$. We will take the $(0, 0, 1)$ face as the Si contact surface. For simplicity of calculation, we assume that there is no bond contraction in the atomic layers paralleled to the contact surface $(0, 0, 1)$. The bond contribution only occurs between the first and the second layers, and between the second and the third layers, as indicated in Fig.3. Under this assumption, the two dimensional periodicity in the direction parallel to the contact surface remains unchanged in the presence of SBR.

By substituting d with $d + \delta d$ into Lennard-Jones potential (Eq.(93)), and expanding the term using polynomial expansion, we obtained the harmonic approximation of Lennard-Jones potential (Eq.(96)), in which the high order terms of δd are ignored.

$$V = -\varepsilon_0 + 36 \frac{\varepsilon_0}{(d_0)^2} \cdot (\delta d)^2 \quad (96)$$

To take SBR into consideration, we need to modify the expression of the harmonic approximation of Lennard-Jones potential for the first three layers, and the inter atomic potential remain unchanged for the inner atoms. In Fig.3, the atomic distance between first and second layer is denoted by d_1 , and d_2 is for the atomic distance between second and third layer. Beyond the third layer, the inter atomic distance is d_0 . By substitution Eqs.(94 and 95) to Eq.(96), the harmonic approximation of Lennard-Jones potential between an atom in layer i and an atom in layer $i+1$ ($i = 1,2$) is then given by

$$V = -\varepsilon_0 \cdot \left(\frac{d_i}{d_0}\right)^{-m} + 36 \frac{\varepsilon_0}{(d_0)^2} \cdot \left(\frac{d_i}{d_0}\right)^{-m-2} \cdot (\delta d)^2. \quad (97)$$

In silicon crystal, the three body interaction contributes significantly to the dynamical matrix. Here, we use the Eq.(98) to model the three body interaction, which is expressed in terms of the bond angle deformation $\delta\theta$. The front constant C in Eq.(98) is taken from Mingo's work[42].

$$V = \frac{1}{2} C \cdot (\delta\theta)^2. \quad (98)$$

3.1.3 Dynamical matrix of thermal contact

As mentioned in chapter 2, dynamical matrix describes the interaction between atoms and is constructed by the second derivative of potential energy with respect to the space coordinates. With the potential energy expression given by Eqs.(97 and 98), the elastic constant between any pair of atoms is determined. These elastic constants are then used to construct the dynamic matrix.

Figure 4: First Brillouin zone and unit cell of (0,0,1) surface in F.C.C crystal structure.

In the semi-infinite thermal contact, there are infinite number of atoms. The dimension of dynamical matrix is infinite, if it is constructed in real space. To reduce the dimension, we consider the phonon mode having wave vector k . With that, the atoms in the layer parallel to the contact surface are identical, hence it is possible to use one atom to represent the whole layer. With considering the nearest neighbor, Atom 0 is used to represent the whole layer, and the wave vector k runs for the whole Brillouin zone of the plane parallel to the contact surface, shown in Fig.4. If the elastic constant tensors between atom 0 and atom i ($i = 0, 1, 2, 3, 4$) are $D_{nn}(a_i)$, where a_i is the displacement of atom i from atom 0, the dynamical matrix of the n^{th} layer denoted by D_{nn} is then given by

$$D_{nn} = \sum_i D_{nn}(a_i) \exp(ik \cdot a_i). \quad (99)$$

Similarly, the dynamic matrices of between two layers denoted by D_{mn} are determined in the same manner.

We select the position of the atom to represent the layer in the way that a saw-tooth atomic chain is formed, as shown by the red-line in Fig.5. With that, the dynamical matrix of the thermal contact for the phonon modes k , is identical to the dynamical matrix of the saw-tooth atomic chain.

Figure 5: Conversion of semi-infinite thermal contact to saw-tooth atomic chain.

3.1.4 Green's function at contact surface

Although, the thermal contact is reduced to a one-dimensional atomic chain, the dynamical matrix is still in infinite dimension. However, since we are only concerned about the transport property of the whole wire, we just need to know the Green's functions near the contact surface, which are used to determine the self-energy of whole atomic wire.

Considering an isolated thermal contact, the coupling between the wire and contact is ignored, hence no self-energy, the retarded Green's function of the contact, which is represented by a saw-tooth atomic chain, is

$$g_{1D}(\omega) = (m \cdot \omega^2 + D_{1D})^{-1}. \quad (100)$$

In Eq.(100), the dynamical matrix of the saw-tooth chain D_{1D} is constructed as follow:

$$D_{1D} = \begin{bmatrix} D_{00} & D_{01} & 0 & 0 & \dots \\ D_{10} & D_{11} & D_{12} & 0 & \dots \\ 0 & D_{21} & D_{22} & D_{23} & \dots \\ 0 & 0 & D_{32} & D_{33} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix}, \quad (101)$$

where D_{mn} is the dynamical matrix between layer m and layer n .

Because we have considered the SBR effect, we intend to determine the Green's functions for the first three layers, which are the first three elements of Green's function in Eq.(100). The surface Green's function can be determined by decimation method, which is explained as follow. Firstly, we select column one of the Green's function g_{1D} (for demonstration purpose, same method applied for other columns), Eq.(100) is expanded into an infinite number of equations as shown:

$$\begin{aligned} (m \cdot \omega^2 + D_{00})g_0 + D_{01}g_1 &= I & (102) \\ D_{10}g_0 + (m \cdot \omega^2 + D_{11})g_1 + D_{12}g_2 &= 0 \\ D_{21}g_1 + (m \cdot \omega^2 + D_{22})g_2 + D_{23}g_3 &= 0 \\ &\dots\dots \end{aligned}$$

After that, the equations on even row can be decimated by expressing the middle elements of the Green's function in the form of the other two elements, and substituted into other equations. For example, the middle elements of the Green's function in the second row is g_1 , which can be expressed as:

$$g_1 = (m \cdot \omega^2 + D_{11})^{-1}(-D_{12}g_2 - D_{10}g_0). \quad (103)$$

Then, the expression of g_1 (Eq.(103)) is substituted into the first equation and the third equation, and, the second equation is eliminated. The remaining equations are

rearranged as the format before decimation. For example, the first equation becomes

$$AG_0 + BG_2 = I. \quad (104)$$

Second round of decimation is then carried out to the even row of the remaining equations. Here, as we only consider SBR in the first three layers, so the dynamic matrix after the third layer are the same. The decimation is carry on until the factor B is very small. With decimation method, the Green's function in the first three layers, together with the Green's function deep inside the thermal contact (, regarded as the Green's function of bulk silicon) are obtained.

3.1.5 Self-energy of LD and RD regions

To take into account the non-equilibrium effect in the region near the coupling point, we take LD and RD regions out from thermal contacts and treat them as a part of atomic wire. The self-energies of LD and RD (denoted by Σ_{LD} and Σ_{RD}) are describing the coupling of the whole wire to the remaining part of the thermal contact. In order to determine the Green's function of the whole wire, Σ_{LD} and Σ_{RD} are required.

With the Green's Function of first three layers determined previously, the Green's Function of LD region g_{LD} can be constructed by Bloch theorem. Meanwhile, the dynamic matrix of LD region D_{LD} is formed by determining the elastic constant tensor. By using the Green's Function of LD region:

$$g_{LD} = (m \cdot \omega^2 + D_{LD} - \Sigma_{LD})^{-1}, \quad (105)$$

the self-energy of LD is given as:

$$\Sigma_{LD} = m \cdot \omega^2 + D_{LD} - g_{LD}^{-1}. \quad (106)$$

The self energy of RD region is determined the same manner.

By the way, with the Green's function of the first three layers, the phonon density of states on the layer i ($i = 1, 2, 3$) are given by following equation:

$$DOS_i = \frac{1}{\pi} \text{Im}[g_{i,i}(\omega)]. \quad (107)$$

3.1.6 Green's Function of whole wire

To consider phonon transport in the whole atomic wire, non-equilibrium Green's Function method is used. If we only consider the ballistic phonon transport, the retarded Green's Function $G_W^R(\omega)$ of the whole wire is:

$$G_W^R(\omega) = [M \cdot \omega^2 + D - \Sigma_{LD}^R(\omega) - \Sigma_{RD}^R(\omega)]^{-1}, \quad (108)$$

where the dynamical matrix of the whole atomic wire D is constructed in the following way:

$$D = \begin{pmatrix} D_{LD} + \Delta_L & D_{LD,W} & 0 \\ D_{W,LD} & D_W & D_{W,RD} \\ 0 & D_{RD,W} & D_{RD} + \Delta_R \end{pmatrix}. \quad (109)$$

Previously, we have mentioned the coupling between original atomic wire and the region LD (RD) are denoted by t_l and t_r as shown in Fig.2. The term Δ_L in Eq.(109) represents the contribution from t_l to D_{LD} , similar to Δ_R . The off-diagonal terms $D_{LD,W}$ and $D_{W,LD}$ are the coupling matrices between region LD and whole atomic wire due to t_l . The terms $D_{W,LD}$ and $D_{RD,W}$ have similar meaning.

With the retarded Green's function, the broadening functions (Γ_L for the left contact and Γ_R for the right contact) and the advanced Green's function G^A are determined:

$$\Gamma_L = -2 \text{Im}[\Sigma_{LD}^R(\omega)], \quad (110)$$

$$\Gamma_R = -2 \text{Im}[\Sigma_{RD}^R(\omega)], \quad (111)$$

$$G^A = (G^R)^\dagger. \quad (112)$$

The phonon transmission of the system is

$$\xi(\omega) = Tr[\Gamma_L(\omega)G_W^R(\omega)\Gamma_R(\omega)G_W^A(\omega)] . \quad (113)$$

Thus, the thermal conductance then is determined in the following way:

$$\sigma = \frac{1}{2\pi} \int_0^\infty d\omega \cdot \hbar\omega \cdot \xi(\omega) \cdot \frac{\partial f}{\partial T} . \quad (114)$$

Finally, we could study the non-equilibrium thermal properties in the region LD (which is assumed at a higher temperature than RD) based on the Green's function of the whole wire. The phonon number on an atom in region LD is given by

$$\rho_j(\omega) = i \cdot \hbar \cdot G_{jj}^<(\omega). \quad (115)$$

Also, the heat currents between atom i and atom j is

$$J_{ij}(\omega) = \frac{1}{2} \hbar\omega \cdot \text{Re}\{Tr[D_{ji} \cdot G_{ij}^<(\omega) - D_{ij} \cdot G_{ji}^<(\omega)]\}. \quad (116)$$

3.1.7 Equilibrium Assumption in LD and RD Regions

In most of the cases, one would assume that there is no temperature gradient in the silicon contacts around the contact interfaces for simplicity of physical analysis on phonon transport. In this case, it is not necessary to introduce in the regions LD and RD. With this simplification, the coupling self energies $\Sigma_{LD}^R(\omega)$ and $\Sigma_{RD}^R(\omega)$ are replaced by

$$\Sigma_{LD}^R(\omega) = t_l^2 \cdot g_{0,0}(\omega), \quad (117)$$

$$\Sigma_{RD}^R(\omega) = t_r^2 \cdot g_{0,0}(\omega), \quad (118)$$

respectively, where the Green's Function of the atom at contact surface and coupled to the wire through the force constant by t_l or t_r is determined by decimation method. Then, the following procedures, such as calculating transmission and thermal conductance, are same as mentioned in previous sections.

3.1.8 Green's function with anharmonic effect

To take the anharmonic effect (due to nonlinear interactions) into consideration, high order terms of Lennard-Jones Potential should be taken into the calculation. These high order terms are present in the form of self-energy in Green's function. Here, the higher order terms are considered up to third order. Hence, the self-energy of third order term $\Sigma_{M(3)}^R(\omega)$ appeared in Green's function. Then retarded Green's function for the whole wire is determined by the following formula:

$$G_W^R(\omega) = [M\omega^2 + D - \Sigma_{LD}^R(\omega) - \Sigma_{RD}^R(\omega) - \Sigma_{M(3)}^R(\omega)]^{-1}. \quad (119)$$

Here, we use a self-consistent method and formula derived from perturbation theory to determine the Green's function of the whole wire[32]. Firstly, we assume the term $\Sigma_{M(3)}^R(\omega)$ is zero, the retarded Green's function is determined by Eq.(119). Also, the lesser and greater Green's Function ($G_W^>(\omega)$ and $G_W^<(\omega)$) are given by:

$$G_W^>(\omega) = G_W^R(\omega)[\Sigma_{LD}^>(\omega) + \Sigma_{RD}^>(\omega) + \Sigma_{M(3)}^>(\omega)]G_W^A(\omega), \quad (120)$$

$$G_W^<(\omega) = G_W^R(\omega)[\Sigma_{LD}^<(\omega) + \Sigma_{RD}^<(\omega) + \Sigma_{M(3)}^<(\omega)]G_W^A(\omega). \quad (121)$$

In the above expression, $\Sigma_{LD, RD}^<(\omega)$ ($\Sigma_{LD, RD}^>(\omega)$) are the well known lesser (greater) self energies due to coupling between the wire W and the contacts. With $G_W^>(\omega)$ and $G_W^<(\omega)$, the lesser than and greater self-energy of the third order term are determined by

$$[\Sigma_{M(3)}^<(\omega)]_{i,j} = \frac{1}{2}i\hbar \sum_{k,l,k',l'} \int_{-\infty}^{\infty} [V_{i,k,l}''' G_{k,k'}^<(\omega') G_{l,l'}^<(\omega - \omega') V_{k',l',j}''' d\omega'], \quad (122)$$

$$[\Sigma_{M(3)}^>(\omega)]_{i,j} = \frac{1}{2}i\hbar \sum_{k,l,k',l'} \int_{-\infty}^{\infty} [V_{i,k,l}''' G_{k,k'}^>(\omega') G_{l,l'}^>(\omega - \omega') V_{k',l',j}''' d\omega']. \quad (123)$$

And finally, the real part and imaginary part of $\Sigma_{M(3)}^R(\omega)$ are calculated:

$$\begin{cases} Im[\Sigma_{M(3)}^R(\omega)] = \frac{\Sigma_{M(3)}^>(\omega) - \Sigma_{M(3)}^<(\omega)}{2i} \\ Re[\Sigma_{M(3)}^R(\omega)] = \int P(\frac{1}{\omega - \omega'}) \cdot \frac{-1}{\pi} Im[\Sigma_{M(3)}^R(\omega')] d\omega', \end{cases} \quad (124)$$

With the Green's function of the whole atomic wire, the heat current I due to phonon transport is given by the general formula

$$I = \frac{-\hbar}{4\pi} \int d\omega \cdot \omega \cdot \text{Tr}[\Sigma_L^<(\omega)G_W^>(\omega) - \Sigma_L^>(\omega)G_W^<(\omega)], \quad (125)$$

hence the thermal conductance σ ,

$$\sigma = \lim_{T_L \rightarrow T_R} \frac{1}{T_L - T_R} \frac{1}{2\pi} \int_0^\infty d\omega \cdot \omega \cdot \text{Tr}[\Sigma_L^<(\omega)G_W^>(\omega) - \Sigma_L^>(\omega)G_W^<(\omega)]. \quad (126)$$

By substituting the terms $G_W^>(\omega)$ and $G_W^<(\omega)$ in the aboved equation using Eqs.(120 and 121), thermal conductance can be expressed in the following way for the purpose of analyzing the effect of nonlinear interaction on phonon transport:

$$\sigma = \sigma_1 + \sigma_2, \quad (127)$$

where

$$\sigma_1 = \frac{1}{2\pi} \int_0^\infty d\omega \cdot \hbar\omega \cdot \xi(\omega) \cdot \frac{\partial f}{\partial T}, \quad (128)$$

$$\sigma_2 = \lim_{T_L \rightarrow T_R} \frac{1}{T_L - T_R} \frac{1}{2\pi} \int_0^\infty d\omega \cdot \hbar\omega \cdot \text{Tr}[\Sigma_L^<(\omega)G_W^R(\omega)\Sigma_{M(3)}^>(\omega)G_W^A(\omega) - \Sigma_L^>(\omega)G_W^R(\omega)\Sigma_{M(3)}^<(\omega)G_W^A(\omega)]. \quad (129)$$

For Eq.(128), it is the same as Eq.(114), $\xi(\omega)$ is transmission function of ballistic phonon transport. In Eq.(129), T_L and T_R are the temperatures of the left and right thermal contact, respectively. σ_1 is considered as the ballistic conductance and σ_2 is interpreted as the correction to σ_1 in the presence of anharmonicity.

3.2 Effect of surface bond reconstruction

Without loss of generality, we consider an atomic wire which consists of two Si atoms. Due to the fact that the atom at the left end of the wire is coupled to the left Si contact

by several bonds, similar condition applies to the atom at the right end of the wire. However, there is only a single bond between the two atoms in the wire. Therefore, we expect the coupling bond strengths between the atoms to the contacts to be much stronger than the bond strength between the two atoms. This can be effectively modeled by three coupling force constants t_l , t_r and t_m , by setting t_l and t_r being much greater than t_m , where t_l is the coupling force constant between the atom at the left end of the wire and atoms on the left contact surface, t_r is for the right side, and t_m is the coupling force constant between the two atoms of the wire. We assume that the atoms in the wire only oscillate in the direction along the wire, for convenience of calculation. We will use $t_l = t_r = 3.16 \text{ eV}/\text{\AA}^2$ and $t_m = 0.316 \text{ eV}/\text{\AA}^2$ [42]. The bulk Si single bond strength, the bulk Si bond length and the elastic force constant for the bond angle deformation C (Eq.(98)) are set equal to 0.682 eV, 2.35 Å [32] and 1.07 eV [42], respectively. To consider the non-equilibrium thermal properties in thermal contact near the contact points, the regions LD and RD in thermal contacts are taken out and treated as parts of the whole wire.

3.2.1 Phonon density of states

From Eq.(107), phonon DOS for bulk and for the first three atomic layers of the silicon contact are shown in Fig.6. For the surface phonon DOS in the absence of SBR (shown by Fig.6b), the high frequency peak should be due to those atomic oscillations which cause significant bond deformation. And the lower surface phonon frequencies originate from the atomic oscillations which cause comparably smaller bond deformation. Thus, atomic oscillations in directions parallel to the atomic planes (which are paralleled to the contact surface $(0, 0, 1)$) are of high frequencies, while for those atomic oscillations in directions perpendicular to the atomic planes the frequencies are lower. We obtain from Fig.6b important information on the effect of SBR on the surface phonon DOS: the presence of SBR eliminates the high frequency

Figure 6: Density of states for a) bulk Si, b) first atomic layer, c) second atomic layer, d) third atomic layer. The solid line corresponds to the case without surface bond contraction, and the dashed line corresponds to the case with surface bond contractions at the Si contact surface.

peak (at around 92 THz) and causes a blue shift for the surface phonon DOS, in the sense that the surface phonon DOS is weakened for frequencies less than 20 THz and enhanced for frequencies between 20 THz and 50 THz. The elimination of the high frequency peak at 92 THz by SBR is expected because SBR leads to a discontinuity of bond strength in the normal direction to the contact surface (from ε_0 in the bulk to $\varepsilon_0 \cdot (\frac{d_i}{d_0})^{-m}$ near the contact surface). This suppresses the high frequency oscillations parallel to the atomic planes which are parallel to the contact surface $((0,0,1))$. The blue shift for the surface phonon DOS is due to the strengthened bond strength $\varepsilon_0 \cdot (\frac{d_i}{d_0})^{-m}$ among the first three atomic layers near the contact surface. The strengthened bonds near the contact surface raise the frequency of the surface phonons at the contact surface. It is then expected that the surface phonon DOS is weakened for low frequencies and enhanced for higher frequencies, that is, a blue shift for the surface phonon DOS occurs.

The disappearance of the high frequency peak at 92THz in the presence of SBR does not affect the thermal conductance, because of the relatively lower oscillation

Figure 7: Transmission function for the case, that is, both the regions LD and RD are in thermal equilibrium. (a) Total transmission function, (b) Contribution of $\vec{k}_{||} = 0$ to transmission function, (c) Contribution of $\vec{k}_{||} = \frac{\pi}{a}(0, 0.5)$ to transmission function, (d) Contribution of $\vec{k}_{||} = \frac{\pi}{a}(0.5, 0.5)$ to transmission function. 'a' is the lattice constant for Si.

frequencies in the atomic wire. However, the blue shift for lower surface phonon frequencies certainly has a significant effect on phonon transport.

3.2.2 Phonon transmission

Due to the two dimensional periodicity in the direction parallel to the contact surface (called the transverse direction), Bloch vectors $\vec{k}_{||}$ exist in that direction. In principle, the contributions to the surface Green's Function $g_{0,0}(\omega)$ from various Bloch vectors $\vec{k}_{||}$ can be calculated by decimation method. We can then determine the contribution of 200×200 $\vec{k}_{||}$ to the broadening function $\Gamma_L(\omega)$, which is determined by Eqs.(110 and 111). And hence, the transmission function $\xi(\omega)$ given by Eq.(113) is determined.

In Fig.7a, the total transmission $\xi(\omega)$ is plotted against frequency ω . And in Fig.7b-d, the contributions from various $\vec{k}_{||}$ to $\xi(\omega)$ is plotted. We see from Fig.7a that the blue shift for surface phonon DOS also causes a blue shift for the transmission

function, as expected. Fig.7b shows that SBR generates a propagating transmission peak at a higher frequency (around 50 THz) for the incident phonons (from deep inside the contact) propagating in the normal direction (i.e., perpendicular to the contact surface), which correspond to $\vec{k}_{||} = 0$. This demonstrates that the strengthened bonds near the contact surface by SBR raises the frequency of the incident phonons propagating in the normal direction ($\vec{k}_{||} = 0$) towards the contact surface. On the other hand, Fig.7c and Fig.7d tell us that the transmission peaks above 20 THz are enhanced by SBR for the incident phonons propagating in the transverse direction (i.e., parallel to the contact surface). This demonstrates that strengthened bonds near the contact surface enhance the DOS of the incident phonons propagating in the transverse direction. The surface phonon DOS consists of contributions from incident phonons propagating in the normal and transverse directions. The effect of SBR on the incident phonons shown by Figs.7b-d leads to the blue shift for the surface phonon DOS (Fig.6b) or the total transmission function (Fig.7a).

3.2.3 Thermal conductance by phonon

The thermal conductance in a silicon atomic wire is calculated from Eqs.(114) (with the region LD and RD being treated as parts of the whole wire). The thermal conductance result, in Fig.8, shows that for sufficiently low temperatures, the conductance is slightly decreased in the presence of SBR. This is due to the reduction of the transmission function by SBR for low frequencies, which are dominant at low temperatures. We also see from Fig.8 that for sufficiently high temperature, the thermal conductance is significantly increased by SBR: the saturation value of thermal conductance (at high temperature) increases by around 30% in the presence of SBR. As we have pointed out above, SBR enhances the transmission function at higher phonon frequencies which are dominant at sufficiently high temperatures. It is then expected that the conductance is increased by SBR for sufficiently high temperatures.

Figure 8: Thermal conductance in a Si atomic wire due to phonon transport.

3.2.4 Passivation of dangling bonds

If passivation of dangling bonds occurred, the blue shift in surface phonon DOS is weakened. This is because on the silicon contact surface, each silicon atom has two dangling bonds. With the passivation of dangling bonds, the two electrons from each surface silicon atom participate in the two new bonds formed. The bond strength between the surface layer and the second layer is reduced, as the attractive force between the two electrons and the Si atoms on the second layer is decreased due to their increased separation. Hence, the effect of SBR on thermal conductance is weakened by passivation of dangling bonds.

3.2.5 Local currents in LD region

Besides the thermal conductance, we also calculated the local heat currents between any two atoms in the thermally non-equilibrium region LD in the left contact which is at 300.1 K (right contact is at 300 K). In Fig.9, the atom labeled by “1” is coupled to the atom at left end of the atomic wire by strength t_l . The deep red heat currents (that is, heat currents of considerable magnitude) around the atom 1 imply that the

Figure 9: Local heat currents between any two atoms in the region LD for a) the case of no SBR, and for b) the base of SBR. The magnitude of the local heat currents are represented by red color: slight red means weak current and deep red means strong current.

temperature gradient mainly exists around the contact interface, as expected. We see from the figure that SBR enhances the thermal current, that is consistent with our previous conclusion. A detailed analysis shows that all the local currents are due to lower frequency phonons. This again is consistent with the fact that the oscillation frequency of the atomic wire is not high (much less than 100 THz).

3.2.6 Variation in length, coupling strength and stiffness

For wire with more than two atoms, the phonon frequencies in the wire are restricted to the range $0 < \omega < \omega_{\max}$. The maximum frequency $\omega_{\max}$ is given by

$$\omega_{\max} = 2\sqrt{\frac{t_m}{m}}, \quad (130)$$

where m is the mass of a silicon atom. For $t_m = 0.316 \text{ eV/\AA}^2$, $\omega_{\max}$ is equal to 21 THz, as shown in Fig.10. When SBR is present, the blue shift in phonon DOS in the contact reduces the transmission probability for the range $0 < \omega < 21 \text{ THz}$ (Fig.6b). We should expect that the conductance is reduced by SBR. This is consistently shown

Figure 10: Thermal conductance with various atomic wire length. Result is obtained under the condition, $t_m = 0.316 \text{ eV/\AA}^2$, $t_{r,l} = 3.16 \text{ eV/\AA}^2$ and $T = 300 \text{ K}$.

by Fig.10. However, when there are only two atoms in the wire, higher frequency ($\omega_{\text{max}} > 21 \text{ THz}$) contributes to the phonon transport. Furthermore, in that frequency range, the transmission probability is enhanced by the SBR. We then conclude that the conductance for two atoms in the wire is increased by SBR and this is also consistent with Fig.10.

The thermal conductance by phonon of the atomic wire is closely related to the stiffness t_m of the wire. When t_m is increased, higher phonon frequencies are allowed to transmit through the wire, that increases the phonon conductance. As is mentioned above, for the wire with more than two atoms, the upper limit of the wire's phonon frequency ω_{max} is approximated by the Eq.(130). Thus smaller t_m restricts the transmission probability leading to a smaller conductance. Fig.11 shows that the transmission is nearly zero in high frequency ($\omega > 21 \text{ THz}$) for the case of five atoms, when $t_m = 0.316 \text{ eV/\AA}^2$. This is consistent with the maximum frequency $\omega_{\text{max}} = 21 \text{ THz}$ determined by Eq.(130). For very small t_m , we expect that the conductance is decreased by SBR, because the blue shift in the DOS of thermal contact reduces the transmission probability for sufficiently low frequencies.

Figure 11: Transmission probability with $t_m = 0.316 \text{ eV/\AA}^2$, $t_{r,l} = 3.16 \text{ eV/\AA}^2$, the highest frequency is around 21 THz.

Meanwhile, the coupling strength between the wire and the thermal contacts (t_l and t_r) affects the phonon transmission in the wire. Physically, we expect that the larger the coupling strength is, the higher the incident phonon frequencies that can transmit through the wire. Fig.12 shows that conductance increases when the coupling strength is increasing from zero to very small values. However, sufficiently large coupling strength will change the phonon density of states in the wire via the self-energies (due to coupling), and this prevents the increments of conductance with higher coupling strength. Fig.12 actually shows that conductance will drop first and then approach a constant value when the coupling strength continues to increase. This is because, when the coupling strength is close to the stiffness of the wire, a maximum peak is produced. With further increase in coupling strength, the conductance is limited by the stiffness of the wire.

From the discussions above, we conclude that t_l , t_r and t_m behave like a filter for phonon transmission in the wire. And for very small coupling strength and stiffness, the conductance is reduced by SBR. In the presence of SBR, surface phonon DOS at the contact surface (Fig.6b) is strongly modified (blue shift and disappearance of the

Figure 12: Thermal conductance with the change of coupling between the wire and silicon surface, with fixed $t_m = 1$ eV/Å².

very high frequency peak at 92 THz). For the case of two atoms in the wire, and for the bond range $0.3 \text{ eV/Å}^2 < t_m < 6.5 \text{ eV/Å}^2$ and $0.3 \text{ eV/Å}^2 < t_{r,l}$, our calculations show that SBR increases the conductance.

3.2.7 Anharmonic effect in the wire

Important information on phonon transport in an atomic wire can be obtained from the transmission function and thermal conductance. We have carried out numerical computations for the transmission function and thermal conductance of a Si atomic wire in order to analyze the effect of SBR on the phonon transport properties in the presence of nonlinear interaction.

Without loss of generality, we also considered an atomic wire which consists of two Si atoms. Due to the fact that the left (right) end atom of the wire is coupled to the left (right) Si contact by several bonds, while there is only one single bond between the left and right end atoms, the bond strength of the left and right coupling bond to the contacts should be much stronger than the strength of the bond between

the two atoms (central bond) of the wire. This can be effectively modelled by three coupling force constants t_l , t_r and t_m , with t_l and t_r being much greater than t_m , where t_l (t_r) is the coupling force constant between the left (right) end atom of the wire and an atom on the left (right) contact surface, and t_m is the coupling force constant between the two atoms of the wire. Furthermore, due to the much stronger left and right coupling bond strengths compared to the central bond, the fluctuations of the left and right coupling bond lengths should be much smaller compared to that of the central bond length. Therefore, it is physically more meaningful to have an anharmonic central bond and treat the surface-atomic-wire bond as harmonic[32].

We assume that the atoms in the wire only oscillate in the direction along the wire, for convenience of calculation. We will restrict our discussion to the lowest order of anharmonicity: V''' . For Lennard-Jones potential V , we have $V''' = (8.94/\text{\AA}) \times V''$ [32], where V'' is set equal to the central bond strength t_m of the atomic wire. We used $t_l = t_r = 3.16 \text{ eV}/\text{\AA}^2$ and $t_m = 0.316 \text{ eV}/\text{\AA}^2$. The bulk Si single bond strength ε_0 , the bulk Si bond length d_0 and the elastic force constant for the bond angle deformation C in Eq.(98)) are set equal to 0.682 eV, 2.35 \AA and 1.07 eV, respectively[32, 42].

Fig.13a shows the temperature dependence of the relative change in thermal conductance σ due to the presence of anharmonicity, for both cases of SBR and of no SBR. We see from the figure the roughly linear relationship between the relative change in σ and the temperature. This is similar to the result of Mingo, which corresponds to the case that SBR is absent and regions LD and RD are assumed to be in thermal equilibrium[32]. We also see that the slope of the line as well as the magnitude of the relative change in σ are increased by the presence of SBR. Figs.13b and c tell us that the thermal conductance of the atomic wire σ is generally decreased by the presence of anharmonicity, whether or not SBR exists. This is expected as nonlinear interaction usually causes scatterings of phonon waves leading to smaller thermal

Figure 13: (a) Relative decrease in thermal conductance of the atomic wire due to anharmonicity, as a function of temperature, (b) Thermal conductance of the atomic wire due to the harmonic approximation of the Lennard-Jones potential, as a function of temperature, (c) Thermal conductance of the atomic wire in the presence of anharmonicity, as a function of temperature, (d) The thermal conductance σ_1 calculated from the first term of Eq.128, as a function of temperature, (e) The thermal conductance σ_2 calculated from the second term of Eq.129, as a function of temperature.

conductance. Furthermore, Fig.13c indicates that in the presence of nonlinear interaction SBR increases the conductance for lower temperatures. But it decreases the conductance when the temperature is high enough.

We can understand Fig.13c in the following way. The above discussion about SBR (subsection on SBR) shows that the presence of SBR produces higher frequency peaks in the transmission function due to the strengthened bond strength among the first three atomic layers near the contact surface. The increased bond strength near the contact surface raises the frequency for the incident phonons propagating in the normal direction (that is, in the direction perpendicular to the contact surface). This important fact is demonstrated in Fig.14: the generated transmission peaks are in the range $20 \text{ THz} < \omega < 60 \text{ THz}$.

On the other hand it is plausible to assume that phonons are scattered weakly

(strongly) by nonlinear interaction at sufficiently low (high) temperatures. The reason behind this assumption is that the amplitudes of the atomic oscillations with frequency ω are proportional to $1/(e^{\hbar\omega/kT} - 1)$. Hence, for low temperature T , the oscillation amplitudes are small, leading to weak nonlinear interaction and hence weak phonon scattering. And for high T , the oscillation amplitudes are large, that leads to strong nonlinear interaction and hence strong phonon scattering.

From the two points mentioned above, we see that at low T the transmission peaks generated by SBR are only weakly decreased by the nonlinear interaction, hence thermal conductance is increased by the presence of SBR. But at sufficient high temperatures, the transmission peaks generated by SBR are significantly weakened by nonlinear interaction, so thermal conductance is decreased by the presence of SBR. Actually, Fig.14 also demonstrates the correctness of the assumption that nonlinear interaction scatters weakly (strongly) the phonons at sufficiently low (high) temperatures.

From Figs.14a and 14b, we see that at sufficiently low temperatures such as $T = 100$ K (dominant frequency range is $0 < \omega < 30$ THz) the decrease of the generated transmission peaks by SBR due to phonon scatterings by nonlinear interaction is small. On the other hand, Figs 14c and 14d indicate that at sufficiently high temperature such as $T = 400$ K (dominant frequency range is $0 < \omega < 60$ THz) there is a significant decrease for the generated transmission peaks due to phonon scatterings by nonlinear interaction.

In Figs.13d and 13e, we plot the conductances σ_1 and σ_2 against temperature, respectively, where σ_1 and σ_2 are determined by Eqs.(128 and 129). Our interpretation of σ_1 and σ_2 is given in the following. In the presence of anharmonicity, the thermal conduction in the atomic wire is approximated as a ballistic transport of phonons, with the inclusion of the self energy $\Sigma_{M(3)}^R(\omega)$ (due to nonlinear interaction) into the retarded Green's Function G_W^R of the wire. And σ_1 is the corresponding conductance. And σ_2 is considered as a correction to σ_1 in the presence of anharmonicity

Figure 14: (a) Transmission function at temperatures $T = 100$ K in the absence of SBR, as a function of frequency. The dashed line corresponds to the presence of anharmonicity, and the solid line corresponds to the harmonic approximation of the Lennard-Jones potential, (b) Transmission function at temperatures $T = 100$ K in the presence of SBR, as a function of frequency. The dashed line corresponds to the presence of anharmonicity, and the solid line corresponds to the harmonic approximation of the Lennard-Jones potential. (c) and (d) Similar to (a) and (b), with $T = 400$ K.

which causes scatterings of phonon waves. From Fig.13d the ballistic conductance σ_1 approaches a saturation value at high temperature, as expected. Fig.13e tells us that the conductance correction σ_2 is small at sufficiently low temperatures and it is very significant at sufficiently high temperatures. This once again demonstrates that nonlinear interaction scatter weakly (strongly) the phonon waves at sufficiently low (high) temperature. Finally, we would like to remark that in the low temperature region (below 50 K), the anharmonic effect is negligibly small as shown in Fig.13. Hence ballistic phonon transport is a very good approximation. The low temperature phonon conductance depends on T^3 . This is a consequence of the linear frequency dependence of the surface phonon density of states at the thermal contact surface[32].

The discussions above shows the importance of SBR of contact surfaces on phonon transport in atomic wires. In fact, we see from Fig.13c that the change of σ due to SBR in the presence of nonlinear interaction is significant: around 15% for $100 \text{ K} < T < 200 \text{ K}$. And, from Fig.13b, in the absence of nonlinear interaction, the change of σ due to

SBR is also very significant: greater than 20% for $T > 100$ K. All our results show that SBR has significant effect on phonon transport in atomic wires.

CHAPTER IV

PHONON TRANSPORT IN SILICON NANOWIRE: SIZE AND DOPING

Recent discovery of high thermoelectric (TE) efficiency in Silicon nanowire (SiNW)[1] raises attention on silicon based TE device[76, 77, 78, 79, 80, 81]. Generally, decrease in lattice thermal conductivity (contributed by phonon) is conducive to TE efficiency. With the reduction in diameter, number of phonon modes is decrease, that reduces phonon conductance. In silicon based TE device, Ge atom substitution is an effective method to reduce thermal conductivity[81, 82, 83]. With the size going down to nanoscale, thermal conductance of TE device may vary with the substitution location. Here, we use non-equilibrium Green's function method[32, 33, 55] to study this effect[25].

This is different from the atomic wire discussed in the chapter 3; the atomic wire sandwiched by thermal contacts are replaced by nanowire, which has more than one atom in cross-section view (parallel to contact surface). Furthermore, these atoms are allowed to vibrate in the transverse direction. For simplicity, atoms in Silicon nanowire are assumed to be in crystalline structure, which is F.C.C. structure with the basis of two silicon atoms, and the cross-section of nanowire is in square shape.

4.1 Theory

We considered a SiNW in square shape and its length in three dimensions (l_x , l_y and l_z) are set to multiple integer of a ($= 5.4309 \text{ \AA}$), which is the lattice constant of silicon crystal. Assume, the wire is aligned in z direction. Because of the square shape, l_x is equal to l_y , therefore, we use one variable w ($= l_x = l_y$) to describe the side length

Figure 15: (a): Schematic diagram of the modeled system: a Si nanowire connected to two semi-infinite Si contacts, the parts LD and RD inside contacts are included into the wire. (b): Distribution of atoms for SiNW with $w = a$ and $l_z = 3a$. Both LD and RD region have 9 atoms.

of the square in cross-section. At either end, the wire is coupled to thermal reservoir, which is semi-infinite and made of silicon. The contact surface is set to be the $(0, 0, 1)$ plane of silicon crystal. To take into account the non-equilibrium temperature in the thermal contact near the contact point between the contacts and the wire, we take out certain parts, denoted by LD and RD[20], in the left and right contact, and treated them as parts of the SiNW, as indicated by Fig.15a. Furthermore, we defined LD (RD) as a collection of atoms in the left (right) contact, which are coupled to the atoms in the wire. In this work, we considered atomic potential for the nearest neighbor and the angle deformation between two bonds. Therefore, for a SiNW with $w = 1a$ and $l_z = 3a$, the LD and RD region are defined as shown in Fig.15b. Both LD and RD have 9 atoms, of which 3 atoms lie on the contact surface.

To use the non-equilibrium Green's function method, we need to construct the dynamical matrix D . The element of dynamical matrix for atom i and atom j , $D_{i,j}$ is defined as

$$D_{i,j} = \frac{1}{\sqrt{M_i M_j}} \cdot \frac{\partial^2 E}{\partial d_i \partial d_j}, \quad (131)$$

where E is the total atomic potential, d_i and M_i are the position and mass of atom i . Because atomic positions are defined in three-dimension space, so $D_{i,j}$ is a 3×3 matrix. For the atomic potential, we considered bond stretching and contraction for

the nearest neighbor. In harmonic case, this potential is described by the following equation [84]:

$$\delta E(i, j) = \frac{1}{2} C_0 \frac{(d_{i,j} - d_0)^2}{d_0^2}, \quad (132)$$

where, d_0 is the equilibrium distance and $d_{i,j}$ is the distance between atom i and atom j . By expanding the Lennard-Jones potential (which is very suitable for silicon bonding), we obtained the value 49.1eV for the constant C_0 . Also, we considered the potential due to angular deformation between two atomic bonds, and it is describe by:

$$\delta E(i, j, k) = \frac{1}{2} C_1 (\delta \Theta_{i,j,k})^2, \quad (133)$$

where $\delta \Theta_{i,j,k}$ is the change in the angle formed by the bond i, j and the bond j, k , and the constant C_1 is set to 1.07eV[42].

The self-energy Σ_{LD} describes the coupling between the LD to the remaining part of left contact. To determine it, firstly we calculate the Green function for the first two layer (counted from contact surface) g_s by decimation method[65]:

$$g_s(\omega, \vec{k}_{||}) = \begin{bmatrix} g_{00}(\omega, \vec{k}_{||}) & g_{01}(\omega, \vec{k}_{||}) \\ g_{10}(\omega, \vec{k}_{||}) & g_{11}(\omega, \vec{k}_{||}) \end{bmatrix}, \quad (134)$$

where $g_{00}(\omega, \vec{k}_{||})$ and $g_{11}(\omega, \vec{k}_{||})$ are the Green's function at contact surface and the first layer, $g_{01}(\omega, \vec{k}_{||})$ and $g_{10}(\omega, \vec{k}_{||})$ are the Green's function between the two layers, ω is the vibration frequency and wave vector $\vec{k}_{||}$ is the Bloch vector paralleled to the contact surface (for a specific $\vec{k}_{||}$, the thermal contact is treated in one dimension.). Then, the Green's function of the LD region g_{LD} is constructed by summing over $\vec{k}_{||}$ in the following way[85]:

$$g_{LD}(i, j, \omega) = \frac{1}{N} \sum_{\vec{k}_{||}} g_{j,k}(\omega, \vec{k}_{||}) \cdot e^{-i\vec{k}_{||} \cdot (\vec{R}_i - \vec{R}_j)}, \quad (135)$$

where j and k , the subscript of the Green's function $g_{i,j}$, is equal to 1 or 0, depending on the location of the atom i and j (on surface layer, value is 0). The number

of sampling points in Brillouin zone parallel to contact surface N is set equal to 200×200 .

By constructing the dynamical matrix D_{LD} , the self-energy of LD is determined by:

$$\Sigma_{LD}(\omega) = \omega^2 I - D_{LD} - g_{LD}^{-1}(\omega). \quad (136)$$

Also, Σ_{LD} is identical to Σ_L , the self-energy of the wire due to the left contact, as:

$$\Sigma_L(\omega) = \begin{bmatrix} \Sigma_{LD}(\omega) & 0 \\ 0 & 0 \end{bmatrix}, \quad (137)$$

For harmonic phonon transport, total self-energy of the wire Σ is equal to the sum of Σ_L and Σ_R , where Σ_R is the self-energy of the wire due to the right contact, and is determined in similar way.

Retarded Green's function of the wire is given by

$$G^R(\omega) = [(\omega^2 + \delta i)I - D - \Sigma(\omega)]^{-1}. \quad (138)$$

The advanced Green's Function G^A equals to $[G^R]^\dagger$. The broadening function due to the left contact Γ_L , is determined by

$$\Gamma_L = -2 \text{Im}[\Sigma_L], \quad (139)$$

similarly for that of right contact Γ_R . Then, the phonon transmission function of the wire is obtained by

$$T(\omega) = \text{Tr}[\Gamma_L G^R \Gamma_R G^A], \quad (140)$$

and thermal conductance of the wire K is given by

$$K = \frac{\hbar\omega}{2\pi} \int d\omega T(\omega) \frac{\partial f(\omega, T)}{\partial T}, \quad (141)$$

where f is Bose-Einstein distribution function and T is the temperature.

Figure 16: Phonon density of state for bulk Silicon. Insert: the dispersion relation.

4.2 Result

4.2.1 Density of states

In bulk case, due to the periodicity of atomic structure, each atom has identical potential field. For wave vector k , the dynamical matrix of atom i is

$$D_i(k) = \sum_j D_{i,j} \cdot e^{(i \cdot k \cdot a_{i,j})}, \quad (142)$$

and the corresponding phonon frequency ω is the square root of the eigenvalue of $D_i(k)$. With that, the dispersion relation of bulk silicon is obtained, as shown in the insert of Fig.16. By counting number of phonon modes within a small range of ω , the well known phonon density of states is obtained and shown in Fig.16.

The phonon densities of states is given by the Green's function with the relation

$$DOS = -1/\pi \text{Im}(g(\omega)). \quad (143)$$

In the process of determining the self-energy, we obtained the surface Green's function $g_{00}(\omega)$ and the green function deep inside contact (by decimation method, treated as bulk case). Hence, their DOS profile is calculated and plotted in Fig.17. The bulk

Figure 17: Phonon density of states for surface plane and the plane deep inside contact (treated as bulk case).

DOS in Fig.17 is different from the DOS in Fig.16. This is because Fig.17 refers to the DOS in a plane (regarded as 2D) and Fig.16 is the DOS in crystal (regarded as 3D). For the surface, due to surface atom vibrations, many vibration modes are shifted to lower frequency[41] and the DOS are enhanced.

4.2.2 Size dependence

Phonon transport properties in SiNW is highly dependent on its cross-sectional size. To investigate this problem, we use different w , the side length of the square, for the SiNW. For demonstration purpose, we select w with the values $1a$, $2a$, $4a$ and $6a$, which are corresponding to 0.54nm, 1.08nm, 2.16nm and 3.24nm. Firstly, we obtained the phonon DOS from the dynamical matrix of SiNWs and they are shown in Fig.18. It is obvious that the DOS of SiNW with $w = 6a$ has very similar profile with the DOS in bulk crystal (Fig.16). However, with the decrease in w , phonon DOS is suppressed and the bulk DOS profile is no longer preserved for very small w ($w < 1\text{nm}$). That is because, when w is big enough, large number of atoms is in the cross-sectional plane, that allows the phonon modes in transverse direction. That statement is also true for bulk case, hence the profile of DOS is similar. With the

Figure 18: Phonon DOS of square shaped silicon nanowires with side length $1a$, $2a$, $4a$ and $6a$. ($a = 5.4309 \text{ \AA}$)

decrease in the cross-sectional size, the number of atoms in the cross-sectional plane is reduced, the vanishing of DOS with transverse wave vector destroy the profile of DOS in bulk case.

We then connected these SiNWs with length ($l_z =$) $3a$ to semi-infinite silicon contact at both ends. The phonon transmission of these SiNWs are determined by Eq.(140) and shown in Fig.19. Similar to the conclusion of phonon DOS, with the decrease in the cross-sectional area, number of atom is reducing, which result in the drop of number of phonon modes. Hence, transmission is weakened for narrower nanowire. Also, the transmission profile is not preserved in thin nanowire. That is because the atoms in cross-section are so few that the periodicity of atom arrangement is hardly observed.

In previous work, the linear temperature dependence of thermal conductivity is found in low temperature range (20 to 100 K) for thin silicon nanowires with rough surface and is explained by the frequency dependent phonon-boundary scattering[79]. In this work, the temperature dependence of thermal conductance (Fig.20) is studied

Figure 19: Phonon transmission of square shaped nanowires with length $3a$. The legend denotes the side length of the cross-section of the nanowires.

based on purely ballistic phonon transport in the wire (i.e. without phonon scatterings). The T^3 dependence is observed at low temperature ($T < 20$ K), and the linear temperature dependence is found especially for thin wire ($w = 1a$) in relative higher temperature ($T > 20$ K). This phenomenon can be explained by analyzing phonon modes. The atom at the center of the wire receives phonon wave with relative short wavelength from the atoms in the wire (atoms within the distance $l/2$) and phonon wave with long wavelength from the atoms in the contacts (atoms with the distance more than $l/2$). Compare to the phonon modes in bulk Si (which has T^3 dependence properties for its thermal conductance), the phonon modes corresponding to the lattice points outside the boundary of wire are missing, that depress the thermal conductance due to short wavelength phonon (large wave vector k) significantly, but only slightly affect the thermal conductance due to long wavelength phonon (small wave vector k). In low temperature, the thermal conductance is dominated by long wavelength phonons (with low frequency, as $\omega = c \cdot k$, c is the sound speed), therefore T^3 dependence is expected. When short wavelength phonons (with relative higher

Figure 20: Thermal conductance of squared wire with various side lengths respect to temperature in (a): log scale, (b): linear scale.

energy) contribute to lattice thermal conductance significantly at relatively high temperature, the T^3 dependence of lattice thermal conductance vanishes, and linear T dependence (which is the property of one dimensional system) appears.

To discuss the effect of wires' size on thermal conductance, without loss of generality, the temperature is fixed at 300 K. The thermal conductance decreases almost linearly with the cross-sectional area (w^2), as shown by the dash line in Fig.21. However, the thermal conductance density D_k , defined as K/w^2 , is decreasing dramatically when w is less than 1.5 nm (shown by the solid line in Fig.21). To compare with the bulk case (in which phonon transport is no longer ballistically beyond mean free path), the conductance density in bulk is about $5 \times 10^8 \text{ WK}^{-1}\text{m}^{-2}$, by using thermal conductivity $150 \text{ WK}^{-1}\text{m}^{-1}$ and mean free path 300 nm[86, 87]. The conductance density in bulk case is comparable to the conductance density when w is greater than 1.5 nm. When the wire is too narrow, the conductance density is much smaller than that in bulk case. For example, in the case of $w = 1a$, the thermal conductance K_0 is 50 pW/K, and conductance density $1.7 \times 10^8 \text{ WK}^{-1}\text{m}^{-2}$, which is reduced by 66% from the bulk case. That effect can be explained by the vanishing of transverse phonon mode in very narrow SiNW.

Figure 21: Thermal conductance (Dash Line) and Thermal conductance density (Solid Line) change with cross-sectional area of square shaped SiNW.

4.2.3 Site dependent of Ge atom substitution

In the following, we study the effect of substitution (a) silicon atom(s) in a SiNW with length ($l_z = 12a$) (6.52 nm) and side length ($w = 1a$) (0.543 nm) with (a) germanium atom(s). Similarly, the SiNW is connected to the silicon thermal contacts, and LD (RD) has identical structure as shown in Fig.15b (9 atoms in total, 3 atoms lie on the contact surface). So, the whole wire (including LD and RD) consists of 169 atoms in total, and these atoms are further categorized into 3 groups by the number of bonds with the atoms, which has the value 1, 2 or 4. Atoms with 4 bonds are those interior atoms, while others are surface atoms. Four types of atomic layers in cross-sectional (x-y) plane of the SiNW are shown in Fig.22, with number of bonds indicated. In order to exclude the effect of Ge substitution on contact, the atoms allowed to be substituted are not coupled to contacts, and there are 138 such atoms in the center of the SiNW.

For germanium crystal, the inter-atomic potential is different from silicon. The constant C_0 and C_1 in Eqs.(132 and 133) are 47.2 eV and 0.845 eV for (Ge-Ge) bonding and (Ge-Ge-Ge) angular deformation [54]. For the potential between Si atom and Ge atom, constant C_0 and C_1 are determined by interpolation. C_0 is set to

Figure 22: Four types of atomic layer (cross-section view) in SiNW with $w = 1a$. Number of bonds are indicated for each atom.

Figure 23: Phonon transmission function of SiNW. (a) pristine SiNW; (b) Same as (a) except the scale of the frequency is divided by a factor of 1.64. (c) All atoms which are allowed to be substituted, are substituted by Ge atoms.

48.1 eV (Si-Ge) bonding, and C_1 is set equal to 0.989 eV and 0.9142 eV for (Si-Si-Ge) and (Si-Ge-Ge), respectively.

Due to the fact that silicon and germanium have the same crystalline structure (F.C.C.), there is a close analogy between the transmission functions of a pure SiNW and a pure Ge nanowire. For example, the shapes of the transmission function in the two cases are similar to each other. Also, the frequencies of the transmission peaks of a pristine SiNW are related to that of a pristine Ge nanowire by a scaling factor. Furthermore, the relative transmission peak heights in the two cases are the same. Fig.23a shows the transmission function of a pristine SiNW (without Ge substitution) falls within the frequency range (from 0 to 100 T·rad/s), and Fig.23c

Figure 24: (a): Percentage changes in thermal conductance with different Ge content. Maximum, Mean and Minimum line denotes the variance of thermal conductance. Dash line represents bulk Si-Ge alloy using the data from J.Garg's work[83]. (b): Percentage change in thermal conductance due to single Ge atom substitution with change in z for 3 groups of bond numbers for the substituted atom.

shows the transmission function of a SiNW with complete Ge substitution, (all atoms (138 atoms), which are allowed to be substituted, are substituted) falls within the frequency range (from 0 to 61 T·rad/s). Thus, red-shift of transmission peaks occurs, from the case of Si to the case of Ge. We expect that when the frequency axis in Fig.23a is scaled down by a factor 1.64, which is determined by $\frac{\sqrt{C_0/m_{Si}}}{\sqrt{C_0/m_{Ge}}}$, the locations of the transmission peaks for a Si wire should coincide with that of the Ge substituted wire. This point is confirmed by Fig.23b and Fig.23c. However, the relative transmission peak heights of a Si wire is different from that of a Ge substituted wire. This is expected because the Ge substituted wire is not a pristine Ge wire.

For a single Ge atom substitution in the SiNW, the substitution location is denoted by z coordinate (along the wire direction and start from left contact surface) and the number of bonds on the atom. The percentage changes in thermal conductance with various locations are shown in Fig.24b. Substitution of surface atom (with 1 or 2

bond(s)) reduce conductance by 5% – 15%; substitution of interior atom (with 4 bonds) reduce conductance by 20% – 40%. The reduction is due to the differences in mass and bond strength between Si and Ge, which lead to damping effect: decrease of phonon frequencies in the wire. Interior atom substitution affecting 4 atomic bonds has more impact in vibration modes, leads to stronger damping effect. Moreover, conductance is significantly reduced when substitution location is near the contacts. This is because the substitution causes mismatch in phonon modes between wire and contacts, which enhances phonon reflections at contact surface.

For more atoms substitutions, thermal conductance depends on the substitution locations too. With N ($0 \leq N \leq 138$) atoms being substituted randomly, the corresponding conductance is determined. The maximum, mean and minimum of the change in conductance are obtained for each N , by repeating the substitution 10 times (Fig.24a). The variation in conductance is about 20% for Ge content less than 15%, and 10% for Ge content greater than 15%. From the previous work[83], percentage change in conductance for bulk Si-Ge alloys is indicated by dash line in Fig.24a. Because of the small surface to volume ratio, center atom has higher chance of being substituted in bulk case. However, this is not true in the wire. For these reasons, the dash line is closer to the minimum line when Ge content is less than 10%. With higher Ge content (greater than 20%), an atomic layer (all atoms in cross-sectional plane, as indicated by Fig.22) has higher chance being replaced by Ge atoms, which further reduces the conductance. But, this can never happen in the bulk case. Thus, the dash line become closer to the maximum line. The above discussion also concludes that 17% of Ge substitution is sufficient to reduce thermal conductance of SiNW.

4.2.4 Conclusion

The proportionality between the thermal conductance and the cross-section area vanishes for thin wires due to the significant reduction of phonon modes. Ge atom substitution for interior atom has more impact over surface atom in reducing the thermal conductance. The thermal conductance is with 10% – 20% variation for the wires with equal Ge content. Finally, the thermal conductance is reduced by 80% with 17% of Ge content.

CHAPTER V

PHONON TRANSPORT IN GOLD WIRE WITH BUFFER LAYER

Recently, considerable effort has been devoted to the structural and transport properties of metallic nanowires and atomic chains[43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53]. In practice, the atomic chains are connected to thermal contacts through a buffer layer instead of a direct connection. This problem have not been addressed in any previous reported work. So it is interesting to investigate the fundamental thermal properties induced by phonons in such system. From a theoretical point of view, it is important to establish a realistic model to calculate thermal conductance of an atomic chain, and to provide accurate information on phonon transport.

In this chapter, we adopt non-equilibrium atomic Green's functions[32, 54, 55, 56, 57] by considering ballistic phonon transport to study the thermal transport properties in a system with the presence of buffer layers. The theoretical model is elaborated in theory section (the section 5.1); and interesting results from investigation of the effect of contact interface (or neck region) are discussed in results and discussion section (the section 5.2).

5.1 Theory

5.1.1 Model description

Our modeled system formed by gold atoms is shown in Fig 25, where the atomic chain is connecting semi-infinite thermal contacts through neck regions (also known as buffer layers) at both sides[58]. Gold atoms are in F.C.C. structure inside the semi-infinite contacts, and the contact surface is set to $(0, 0, 1)$ plane. The neck region is

Figure 25: A typical configuration of thermal transport systems. The smaller figure shows the cross section viewed from $[010]$ direction.

assumed in pyramidal form, thus a neck region with N buffer layers is constructed by $(N + 1)^2$ atoms. The notations used in our modeled system are shown in Fig.26, LB (RB) represents thermal contact on left (right), D is the atomic chain and LD (RD) denotes the region connecting the atomic chain and the first buffer layer.

5.1.2 Embedded atom method (EAM)

To investigate phonon transport in the system by non equilibrium Green's function method, we need to know the dynamic matrix. In this work, we confine the motion of the atoms of the atomic chain in the z -direction, but other atoms can move in all direction. And EAM empirical potential was selected to describe the atoms' interaction[59, 60]:

$$K_{ij} = -Q_{ij} - F_i'' \hat{g}_i \hat{r}_{ij} \rho_j^{a'} - F_j'' \hat{g}_j \hat{r}_{ji} \rho_i^{a'} + \sum_{k \neq i, j} F_k'' \rho_j^{a'} \rho_i^{a'} \hat{r}_{jk} \hat{r}_{ik}. \quad (144)$$

The quantities in the above expression are given below:

$$Q_{ij} = \psi_{ij}'' \hat{r}_{ij} \hat{r}_{ij} + \psi_{ij}' (\hat{\mathbf{1}} - \hat{r}_{ij} \hat{r}_{ij}) / r_{ij}, \quad \hat{g}_i = \sum_{s \neq i} \rho_s^{a'}(r_{is}) \hat{r}_{is}, \quad (145)$$

Figure 26: Cases of different number of atomic layers N in the buffer layers, view from $[010]$ direction.

where $\hat{\mathbf{1}}$ is unit tensor, $\hat{r}_{ij}$ and r_{ij} are the unit vector and distance from atom i to atom j , and ψ'_{ij} and ψ''_{ij} are determined by equations:

$$\psi'_{ij} = F'_i(\rho_i)\rho_j^{a'} + F'_j(\rho_j)\rho_i^{a'} + \phi'_{ij}, \quad (146)$$

$$\psi''_{ij} = F'_i(\rho_i)\rho_j^{a''} + F'_j(\rho_j)\rho_i^{a''} + \phi''_{ij}. \quad (147)$$

The embedded atomic function $F_i(\rho_i)$ [59, 60, 61] is:

$$F_i(\rho_i) = -F_0 \left[1 - n \ln\left(\frac{\rho_i}{\rho_e}\right) \right] \left(\frac{\rho_i}{\rho_e}\right)^n + F_1\left(\frac{\rho_i}{\rho_e}\right). \quad (148)$$

where

$$\phi_{ij} = -\phi_0 \left[1 + \beta \left(\frac{r_{ij}}{r_a} - 1 \right) \right] e^{-\beta\left(\frac{r_{ij}}{r_a} - 1\right)}, \quad (149)$$

(Rose-like pairwise interaction potential[61, 62, 63, 64]) and

$$\rho_i = \sum_{j \neq i} \rho_j^a(r_{ij}). \quad (150)$$

The function

$$\rho_j^a(r_{ij}) = \rho_e e^{-\alpha\left(\frac{r_{ij}}{r_e} - 1\right)} \rho_j^a(r_{ij}) \quad (151)$$

is the density tail at site i due to the atom at site j . Parameters of gold atom used in our computation are listed in Table 1. The dynamic matrix of semi-infinite thermal contact is constructed by considering Bloch vectors $\vec{k}_{\parallel}$ (shown in Fig.27) in planes parallel to the contact surface. Thus the semi-infinite thermal contact is divided into many slices. By using decimation method[65] based on the dynamic matrix of thermal contact, the contact surface Green's function D_0 was determined. For dynamic matrix of buffer layers, we considered the nearest and second nearest neighbor interactions.

EAM is a very good potential to describe bulk metal, but it is not accurate for low-dimensional system such as atomic chain. This problem has been pointed out by Peláez and Serena[46]. To overcome this problem, in this work, we adopt bond-order-length-strength (BOLS) correlation premise[66, 67] to obtain an averaged estimation of the equilibrium bond length r_0 , bond energy E_i , and cohesive energy E_{Bi} per atom in the atomic chain. According to BOLS, the bond contraction coefficient $c_i(z_i)$ is given by

$$c_i(z_i) = \frac{2}{1 + e^{\frac{(12-z_i)}{8z_i}}}, \quad (152)$$

where z_i is the effective atomic coordination number, and $z_i = 2$ for atomic chain. The bond energy is determined by $E_i = c_i^{-1}E_b$ and cohesive energy is given by $E_{Bi} = z_i E_i$. The obtained parameters are then substituted into the Rose's universal binding energy[62]. So the inter-atomic potential of atomic chain is expressed:

$$E(r_{ij}) = -E_{Bi} \left[1 + \alpha \left(\frac{r_{ij}}{r_0} - 1 \right) \right] e^{-\alpha \left(\frac{r_{ij}}{r_0} - 1 \right)}. \quad (153)$$

where $E_{Bi} = 1.4628$ eV and $\alpha = 2.5537$ (Values are calculated base on parameters in Reference [53]). Hence, the dynamic matrix of atomic chain is obtained.

5.1.3 Green's function and conductance

The retarded Green's function of the atomic chain is:

$$D_D^r = [\omega^2 - H_{DD} - \Sigma_L^r - \Sigma_R^r]^{-1}, \quad (154)$$

where H_{DD} is the dynamic matrix of the atomic chain and $\Sigma_{L(R)}^r$ is the self-energy due to the coupling between the atomic chain and the LD (RD) region which only has one atom. The effect of buffer layers is involved in the self-energy $\Sigma_{L(R)}^r$, and they are obtained by:

$$\begin{aligned}\Sigma_L^r &= H_{D,LD}(\omega^2 - H_{LD,LD} - \Sigma_L')^{-1} H_{LD,D}, \\ \Sigma_R^r &= H_{D,RD}(\omega^2 - H_{RD,RD} - \Sigma_R')^{-1} H_{RD,D},\end{aligned}\quad (155)$$

where Σ_L' (Σ_R') is the self-energy due to the coupling between LD (RD) region and the first buffer layer in the neck region.

$$\begin{aligned}\Sigma_L' &= H_{LD,C_1} W_{C_1 C_1}^{-1} H_{C_1,LD}, \\ \Sigma_R' &= H_{RD,C_1} W_{C_1 C_1}^{-1} H_{C_1,RD}.\end{aligned}\quad (156)$$

In Eq.(156), H_{LD,C_1} is the coupling between buffer layer (denoted C_1) and the atom in LD ; $W_{C_1 C_1}^{-1}$ is the Green's function of the buffer layer C_1 , in which the coupling between the buffer layer and the left contact is taken into account, as shown:

$$W_{C_1 C_1} = \omega^2 I + \begin{bmatrix} -H_{C_{11},C_{11}} - \Sigma_{0L_1} & -(H_{C_{11},C_{12}} + \tau_{12}) & -(H_{C_{11},C_{13}} + \tau_{13}) & -(H_{C_{11},C_{14}} + \tau_{14}) \\ -(H_{C_{12},C_{11}} + \tau_{21}) & -H_{C_{12},C_{12}} - \Sigma_{0L_2} & -(H_{C_{12},C_{13}} + \tau_{23}) & -(H_{C_{12},C_{14}} + \tau_{24}) \\ -(H_{C_{13},C_{11}} + \tau_{31}) & -(H_{C_{13},C_{12}} + \tau_{32}) & -H_{C_{13},C_{13}} - \Sigma_{0L_3} & -(H_{C_{13},C_{14}} + \tau_{34}) \\ -(H_{C_{14},C_{11}} + \tau_{41}) & -(H_{C_{14},C_{12}} + \tau_{42}) & -(H_{C_{14},C_{13}} + \tau_{43}) & -H_{C_{14},C_{14}} - \Sigma_{0L_4} \end{bmatrix}$$

With non-equilibrium Green's function, the heat current due to phonon transport was determined [68]:

$$J_{L(R)} = \int \zeta(\omega) \hbar \omega [f_L(T_L) - f_R(T_R)] d\omega / 2, \quad (157)$$

where $f_L(T_L)$ and $f_R(T_R)$ are the Bose-Einstein distribution functions in the left and right contacts with the temperature T_L and T_R . The transmission function $\zeta(\omega)$

Table 1: Parameters of gold [61]

Au	
a_0 (Å)	4.08
r_e (Å)	2.885
r_a (Å)	2.4336
F_0 (eV)	3.03
F_1 (eV)	0.4728
ϕ_0 (eV)	0.2774
α	11.5349
β	5.7177
n	0.5
$m(\times 10^{-25}\text{kg})$	3.2702
$\omega_0(\text{THz})$	8.66

Figure 27: a) The direct lattice unit cell in the contact surface, and b) the first Brillouin Zone. a_0 is the lattice constant

is given by: $\zeta(\omega) = \text{Tr}(\Gamma_L D_D^r \Gamma_R D_D^a)$, where $D_D^{r(a)}$ is retarded (advanced) Green's function of the atomic chain, and $\Gamma_{L(R)}$ is the broaden function due to couplings between the atomic chain and the left (right) contact. The thermal conductance κ is calculated according to the definition $\kappa = J/\Delta T$, where ΔT represents a small difference in temperature across the atomic chain, so:

$$\kappa = \int_0^\infty \frac{d\omega}{2} \hbar \omega \left[\frac{\partial f(\omega, T)}{\partial T} \right] \zeta(\omega). \quad (158)$$

In our calculation, all physical quantities were treated as dimensionless, so we paid more attention to the relative changes of physical quantities rather than their absolute values.

Figure 28: a) Bulk density of state of contact, b) Surface densities of states. Blue dashed line is DOS of $g_{xx}(\omega)$ or $g_{yy}(\omega)$ parallel to the contact surface. Red solid line is DOS $g_{zz}(\omega)$ perpendicular to the contact surface.

5.2 Results and Discussions

Base on the theory mentioned above, phonon transport in atomic chains with different number of buffer layers N in the neck region is evaluated. In this section, the results like Density of states (DOS), the transmission and thermal conductance are discussed.

DOS, affecting thermal conductance through self-energy and the transmission function, is a very important physical quantity in phonon transport in the atomic chain. Fig.28a shows the bulk DOS of the gold contacts, which is in good agreement with the well-known experimental result and theoretical predictions[69, 70]. In Fig.28b, the solid line is the partial surface DOS ($g_{zz}(\omega)$) for polarization in z direction, it is obtained by evaluating the Green's function: $g_{zz}(\omega) = -Im[D_{zz}^r(\omega)]/\pi$; the dashed line is the surface DOS ($g_{xx}(\omega)$ or $g_{yy}(\omega)$) for polarization in the x or y direction which is parallel to the contact surface. It is obvious that the shape of $g_{zz}(\omega)$ is different from the bulk DOS, while $g_{xx}(\omega) = g_{yy}(\omega)$ appear in a similar shape with bulk DOS. The DOS of atomic chain (Figs.29A,B,C and D) is modified dramatically in the presence of the contacts coupled to the atomic chain, but the cutoff frequency appeared in all cases, beyond which phonons do not contribute to

Figure 29: The solid lines are DOS of finite atomic chains (7 atoms) for structures a), b), c) and d) in Fig.26. The dashed line in plot A is DOS of the infinite atomic chain.

thermal conductance.

Fig.30 shows thermal conductances of the system with different number of buffer layers ($N = 0, 1, 2, 3$ as shown in Fig.26). The temperature dependence of thermal conductance in nanowire is clearly shown by these curves [31, 71, 72, 73]. At low temperature, thermal conductance shows the linear behavior (proportional to temperature, see the inset of Fig.30), which is consistent with the theoretical prediction[31, 74] and experimental confirmation[75] of the quantized thermal conductance $\pi^2 k_B^2 T / 3h$. The continuous variation of κ with T rather than step-like behavior in charge transport reflects the entropy transport in thermal current. When temperature is sufficiently high, the thermal conductance increases rapidly showing the Debye behavior. This is because more degrees of freedom are excited in the system. At even higher temperature, the thermal conductance approaches a saturation value, as all the excited states are occupied.

From Fig.30, we notice that with the increasing number of buffer layers, the thermal conductance is decreasing. This can be explained from the physical mechanism of

Figure 30: Thermal conductances of different junction configurations. The numbers indicate the structures corresponding to Fig.26. Inset are thermal conductance as a function of buffer layer number N at Debye temperature and low temperature thermal conductance, respectively.

phonon transport. As the contact reservoir injects phonons into atomic chain, according to the transmission function $\zeta(\omega)$, a phonon with the frequency of ω can transmit through the atomic chain whenever a channel mode of that frequency is available. For $N = 0$ (no buffer layer), DOS at the tip of the neck region (i.e. the atom in LD region) consists of a broad range of frequencies, as in shown by Fig.29A. This is due to weak reflections for the incident phonons by the neck region. In this case the surface DOS cover all the peak frequencies in the DOS of atomic chain. Hence phonons are injected into all modes in the atomic chain, leading to high transmission probability (Fig.31a) and large thermal conductance (Fig.30). When N increases from zero, DOS at the tip of the neck region is reduced. As shown in Figs.29B, C and D, the DOS has narrower frequency range and more sharp peaks, that is because incident phonons experienced stronger reflection in the pyramidal neck region. In these cases, DOS does not cover all the peak frequencies in the DOS of the atomic chain. Hence the number of phonons injected into atomic chain is much reduced, leading to low

Figure 31: Transmission probabilities corresponding to system a), b), c) and d) in Fig.26

transmission probability (Fig.31b, c and d) and small thermal conductance (Fig.30).

It is easy to understand why the incident phonons suffer stronger reflection in the neck region when N increases. When the number of buffer layers N increases (the physical size of the pyramidal neck region becomes larger), the incident phonons need to propagate through a longer distance before arriving at the atomic chain. Hence these phonons suffer stronger scattering in the neck region and reflection by the boundary of the neck region. Thus the transmission function is reduced to a finite number of narrow and sharp resonant peaks, that lead to a weak thermal conductance. While N is continuously increasing, at certain sufficiently large value, thermal conductance is expected to approach a small value. And the largest thermal conductance is when $N = 0$. In this case the atomic chain directly connects to 4 surface atoms of the contact. In our calculations, we found that the thermal conductance is sensitive to the bonding in the buffer layers as well.

Finally, we investigated phonon transport for all points in the first Brillouin zone, which is equivalent to all individual phonon incident directions. In Fig.27, the Γ point ($\vec{k}_{\parallel} = 0$) corresponds to the phonon incident direction which is perpendicular to the

contact surface. These phonons experienced less reflections (by the boundary of the neck region) and contribute more to thermal conductance, while phonons in other incident direction (represented by points of $\vec{k}_{||} \neq 0$ in the Brillouin zone) undergo strong reflection and contribute less to thermal conductance.

5.3 Conclusion

In summary, we use the atomic non-equilibrium Green's functions together with EAM and BOLS to investigate phonon transport properties in atomic chain with different number of buffer layers in neck region. The results show that longer neck region in pyramidal form has lower thermal conductance. The reason is that the phonon reflection and scattering are enhanced by the increasing size of the buffer layer.

CHAPTER VI

ELECTRON TRANSPORT IN THERMOELECTRIC DEVICE

Low efficiency in thermoelectric device is the major reason preventing thermoelectric (TE) device from being used widely[88]. The TE efficiency is indicated by the dimensionless TE figure of merit (FOM). In this chapter, we firstly (in section 6.1) revisit the physics of TE effect and discuss the strategy of increasing FOM. To demonstrate the strategy, TE effect in silicon wires is studied using a semi-classical approach[23]. Secondly (in section 6.2), we investigate the influence of electron scattering on TE effect[24]. The scattering effect is modeled by using the concept of Büttiker probe. In the last section (section 6.3), with the understanding of TE effect, we propose a TE device with potential in achieving high FOM.

6.1 The importance of electronic thermoelectric efficiency

The symbols of the quantities frequently used in the discussion are listed in Table 2. The FOM is defined as:

$$ZT = \frac{S^2 T \sigma}{\kappa_l + \kappa_e} = \frac{S^2 T G}{K_l + K_e}. \quad (159)$$

From the above expression, one notices that FOM is related to both charge and phonon transport[89]. In phonon transport, K_l is the only parameter. Reducing K_l is one of the directions to achieve high FOM. However, in charge transport, there are three mutually dependent parameters (S , G , and K_e), which increase the complexity. Here, we propose to use two parameters, electronic TE efficiency ξ and electronic

Table 2: Symbols used in thermoelectric effect

Parameter(s)	Symbol(s)
Figure of Merit	ZT
Seebeck coefficient	S
Peltier coefficient	Π
Electric conductivity/conductance	σ/G
Thermal conductivity/conductance	κ/K
by charge carriers	κ_e/K_e
by phonons	κ_l/K_l
Electronic	
thermoelectric efficiency	ξ
equivalent κ/K	κ_p/K_p
Fermi level	μ
Temperature difference	ΔT

equivalent thermal conductance K_p , to replace these three parameters. After revisiting the power flow in TE device, FOM is expressed in term of powers, and two upper limits of FOM are pointed out. We notice ξ is an important parameter to define the upper limit of FOM for a specific TE device, and is purely determined by a probability distribution function of charge transport.

6.1.1 Power flow in TE device

TE device is a power conversion device, it is important to understand the power flow (Fig.32b). The thermal power across TE device exists in the form of temperature difference and is expended by both phonons and charge carriers. Thermal power expended by phonons is

$$P_{K_l} = K_l \Delta T. \quad (160)$$

Similarly, the thermal power due to thermal conductance by charge carriers is

$$P_{K_e} = K_e \Delta T. \quad (161)$$

The sum of P_{K_l} and P_{K_e} is the rate of thermal energy loss in thermal conduction, and it is the wasted power. The thermoelectric power P_{TE} , which is the mount of thermal power to be converted to electrical power, is the only useful power, To determine the

expression of P_{TE} , we need to understand how electricity is generated from thermal energy.

Generally, TE device is evaluated at open circuit (i.e. $I_e = 0$), zero-biased voltage ($\Delta V = 0$) and non-zero temperature difference ($\Delta T \neq 0$). The thermal reservoirs at both ends of TE device are in thermal equilibrium, and their electron occupation probabilities are given by Fermi-Dirac function:

$$f(E, T) = [\exp(\frac{E - \mu}{k_B T}) + 1]^{-1}, \quad (162)$$

where k_B is the Boltzmann constant. Due to the temperature difference, electron occupation probabilities at two ends of TE device are unequal, which causes a electric current. For the component of the electric current at energy level E , its direction is given by the sign of $(\partial f(E)/\partial T)$, which is an odd function respect to Fermi level. Thus, the component of the current above Fermi level is in the opposite direction of that below Fermi level, as shown in Fig.32c. When one component is larger, a net electric current ($I_{e,T}$) appears, which changes the charge carrier concentrations at both ends of TE device. Hence a potential difference (ΔV) is produced, electricity is then generated.

Because no load is connected to the TE device, the potential difference produces another electric current ($I_{e,V}$) in the opposite direction of $I_{e,T}$ with the same magnitude. This current ($I_{e,V}$) is named the reversed current, with which the net current in the TE device ($I_e = I_{e,T} + I_{e,V}$) is equal to zero, and that satisfy the open circuit condition. The zero net current can be interpreted as the result of the dynamic equilibrium of Seebeck effect and Peltier effect. That is because: the generated electricity could not be delivered to any load (due to the open circuit), the reversed current ($I_{e,V}$) is hence produced and is actually pumping heat from cold end to hot one, which means the generated electricity is used to pump heat and is converted back to thermal energy through Peltier effect. Therefore, the power of Peltier effect P'_{TE} equals to P_{TE} (i.e. $P_{TE} = P'_{TE} = \Pi \cdot I_{e,V}$, where Π is the Peltier coefficient). With

Figure 32: (a): Figure of merit ZT is mapped by A and ξ , where A is the ratio of thermal conductance by phonons K_l over the electronic thermal conductance K_p , and ξ is the electronic thermoelectric efficiency. To achieve $ZT > 1$, the condition $\xi > 0.5$ and $A < 1$ is necessary. (b): Power flow diagram in a thermoelectric device: among the three powers (P_{K_l} , P_{K_e} and P_{TE}), only P_{TE} is used to generated electricity. The expressions ($\frac{1}{A+1}$, $\frac{A}{A+1}$, ξ and $1 - \xi$) indicates the fraction of power flow. (c): The directions of electric current and heat current due to temperature gradient in thermoelectric device at 300 K. Opposite flow direction in electric current for the components above and below Fermi level, result in the reduction in thermoelectric effect.

the relations: $I_{e,V} = -\Delta V \cdot G$ and $S = -\Delta V/\Delta T = \Pi/T$, we then obtained

$$P_{TE} = S^2 T G \Delta T. \quad (163)$$

6.1.2 Reformulate figure of merit

With FOM interpreted as the ratio of useful power over wasted power, by substituting Eqs.(160,161 and 163), the familiar expression

$$ZT = \frac{P_{TE}}{P_{K_l} + P_{K_e}} = \frac{S^2 T G}{K_l + K_e} \quad (164)$$

is obtained. Based on previous work [90], G , K_e and S are given by:

$$G = -I_e/\Delta V|_{\Delta T=0} = e^2 K_0 \quad (165)$$

$$K_e = -I_Q/\Delta T|_{I_e=0} = (K_2 - K_1^2/K_0)/T \quad (166)$$

$$S = -\Delta V/\Delta T|_{I_e=0} = K_1/(eT K_0), \quad (167)$$

where K_n is defined as:

$$K_n = \frac{2}{h} \int T(E) \left(-\frac{\partial f}{\partial E}\right) (E - \mu)^n dE, \quad (168)$$

and e is the charge unit. In Eq.(168), the electron transmission function $T(E)$ can be determined by non-equilibrium Green's function theory (Eq.(169))[35] or Boltzmann theory (equivalent to transport distribution function $\Sigma(E)$) (Eq.(170))[37].

$$T(E) = Tr[\Gamma_L G^R \Gamma_R G^A] \quad (169)$$

$$\Sigma(E) = \sum_{\vec{k}} v(\vec{k})^2 \tau(\vec{k}) \delta(E - E(\vec{k})) \quad (170)$$

With Eqs.(165, 166 and 167), the total thermal power expended by charge carriers is

$$P_{K_e} + P_{TE} = K_p \Delta T, \quad (171)$$

where the electronic equivalent thermal conductance K_p is defined as:

$$K_p = K_2/T = K_e + S^2 T G. \quad (172)$$

Also, FOM is rewritten as

$$ZT = \frac{K_1^2/(K_0 K_2)}{1 - K_1^2/(K_0 K_2) + \kappa_l T/K_2} \quad (173)$$

$$= \frac{\xi}{1 - \xi + A}, \quad (174)$$

with

$$\xi = \frac{K_1^2}{K_0 K_2}; A = \frac{K_l}{K_p}. \quad (175)$$

Hence, FOM is mapped by two parameters[91] A and ξ as shown in Fig.32a.

In fact, it is easy to prove the term ξ in Eq.(174) is defined as the ratio of the thermoelectric power (P_{TE}) over the total thermal power expended by charge carriers ($P_{TE} + P_{K_e}$) by using Eqs.(161, 163, 165, 166, and 167). With that, ξ is the electronic thermoelectric efficiency. It is also easy to prove $0 \leq \xi \leq 1$: by treating the term $T(E)(-\frac{\partial f}{\partial E})$ in Eq.(168) as a probability distribution function (PDF) of the term $(E - \mu)$, then

$$\xi = \frac{P_{TE}}{P_{TE} + P_{K_e}} = \frac{\langle E - \mu \rangle^2}{\langle (E - \mu)^2 \rangle}, \quad (176)$$

which is generally less than one. In Eq.(176), the numerator indicates a symmetric PDF (with respect to Fermi level) gives zero in ξ . This is consistent with previous discussion: thermoelectricity is generated by a net current ($I_{e,T} \neq 0$). So, blocking one component (either below or above Fermi level) of the current is an effective way to enhance ξ . In previous works[92, 93, 94, 95], blocking the current below Fermi level is named "cold electron filtering", and produces the N-type leg of a TE device. To get an even higher ξ , the PDF should be confined within a narrow region ΔE (i.e. the PDF is a sharp peak[96, 97, 98, 99, 100]), as inferred from Eq.(176).

The best thermoelectric device has ξ equals to one and A equals to zero, that means, the PDF is a Dirac delta function[91]. This indicates that the best thermoelectric device is a superconductor at the single energy level, while it is an insulator at other levels. It is unlikely to develop such a device based on current technology,

but it gives an alternative direction of developing high FOM TE device: increasing ξ by engineering the electron transmission function.

6.1.3 Two upper limits of FOM

One has claimed that FOM is bounded by $1/A$ [91]. In our interpretation, this upper limit of FOM is demonstrated in the following way:

$$\begin{aligned} \frac{1}{A} &= \frac{K_p}{K_l} = \frac{K_e + S^2TG}{K_l} \\ &= \frac{P_{TE} + P_{K_e}}{P_{K_l}} \geq \frac{P_{TE}}{P_{K_l} + P_{K_e}} = ZT. \end{aligned} \quad (177)$$

In fact, there are two more strict upper limits, limit 1:

$$ZT = \frac{P_{TE}}{P_{K_l} + P_{K_e}} \leq \frac{P_{TE}}{P_{K_e}} = \frac{\xi}{1 - \xi}, \quad (178)$$

and limit 2:

$$ZT = \frac{P_{TE}}{P_{K_l} + P_{K_e}} \leq \frac{P_{TE}}{P_{K_l}} = \frac{\xi}{A}. \quad (179)$$

Also, these two limits can be proved directly from Eq.(174) with $0 \leq \xi \leq 1$ and $0 \leq A$. FOM approaches limit 1, when K_e is much greater than K_l . This limit is purely defined by ξ , and indicates the maximum FOM can be achieved by the electron transmission function. Limit 2 is a better version of the limit $1/A$, and works in the region when K_l is non-negligible.

6.1.4 TE device with rectangular transmission function

For a TE device with a rectangular transmission function, as shown in Fig.33a, its electronic equivalent thermal conductance K_p and electronic TE efficiency ξ relate to the location E_c of the rectangle and its energy width ΔE , but not the transmission height β . At room temperature (300 K), K_p is large when E_c is small and ΔE is large (Fig.33b). In contrast, ξ is large when E_c is large and ΔE is small (Fig.33c). Thus, we are facing the trade off between power (total thermal power delivered to

charge carriers) and efficiency (electronic TE efficiency). Assume K_l is not negligible, by using the limit 2 (Eq.(179)), FOM can be rewritten as a function of K_l :

$$ZT \leq (K_p \cdot \xi) \cdot (K_l)^{-1}. \quad (180)$$

The term $(K_p \cdot \xi)$ is plotted in Fig.33d, where the optimal region is bounded by the contour line 0.99. In optimal region, the term $(K_p \cdot \xi)$ equals to 216β nW/K, and the optimal region can be simply described by a line equation

$$E_c = 0.02 + \Delta E/2 \quad (181)$$

with ΔE greater than 0.18 eV. That means, the rectangular transmission starts at 0.02 eV, which generates an abrupt PDF to enhance ξ . A wider transmission ($\Delta E \geq 0.18$ eV) is conducive to charge transport, hence increase K_p . The optimal region were plotted in Fig.33b and Fig.33c indicated by E_{op} . From Fig.33c, the optimal region has ξ slightly greater than 0.8. By using the limit 1 (Eq.(178)), FOM in the optimal region is bounded by 4. Higher FOM may be achievable in the upper-left part in Fig.33c, but there are two adverse points: the device is in low power rating and requires very lower K_l , which is difficult to achieve.

6.1.5 Thermoelectricity in silicon nanowire

To demonstrate the optimization of FOM based on ξ and K_p , TE properties of silicon nanowires are investigated. The electron transport properties of silicon nanowires are determined by using Boltzmann theory (Eq.(170)).

With Mathiessen's rule, the total relaxation time is defined as:

$$\tau^{-1} = \sum_i \tau_i^{-1}. \quad (182)$$

The relaxation time τ_{ii} due to ionized impurities, is given by the following equation[101]:

$$\tau_{ii}^{-1} = \frac{e^2 N m^*}{8\pi \epsilon^2 \hbar^3 k^3} \left(\ln \left(1 + \frac{4k^2}{\beta^2} \right) - \frac{4k^2}{\beta^2 + 4k^2} \right). \quad (183)$$

Figure 33: (a): Rectangular shaped transmission function with center located at E_c , energy width ΔE and transmission β ; (b): Normalized K_p (electronic equivalent thermal conductance); (c): ξ (electronic thermoelectric efficiency), and (d): Normalized ($K_p \cdot \xi$) with various ΔE and E_c . The optimal region for the rectangular thermoelectric device is bounded by the contour line 0.99 in (d), which is also plotted in (b) and (c), as indicated by E_{op} .

Table 3: Parameters of Silicon [103, 104]

Parameters	Symbol (unit)	Value
Dielectric constant	ϵ/ϵ_0	11.7
Electron effective mass	m^*/m_e	0.92
Electron deformation potential	$D_A(\text{eV})$	10.5
Hole deformation potential	$D_V(\text{eV})$	4.8
Density	$\rho(\text{kg/m}^3)$	2329
Nonparabolicity	$\alpha(\text{eV}^{-1})$	1.25
Effective sound speed	$v_s(\text{m/s})$	6351

The inverse screening length β is determined by:

$$\beta^2 = \frac{2e^2}{\epsilon k_B T V} \sum_{\vec{k}} f(E(\vec{k}))(1 - f(E(\vec{k}))), \quad (184)$$

where V is the volume. The relaxation time τ_{DP} for phonon deformation-potential[102] is

$$\tau_0^{-1} = \frac{\pi k_B T D_A^2}{\rho v_s^2 \hbar} D(E), \quad (185)$$

$$\tau_{DP}^{-1} = \tau_0^{-1} \left\{ \left[1 - \frac{\alpha E}{1 + 2\alpha E} \left(1 - \frac{D_V}{D_A} \right) \right]^2 - \frac{8}{3} \frac{\alpha E (1 + \alpha E)}{(1 + 2\alpha E)^2} \frac{D_V}{D_A} \right\}, \quad (186)$$

where E is the energy relative to the band edge, and $D(E)$ the density of states. The relaxation time τ_{gb} due to the grain boundary scattering is

$$\tau_{gb}^{-1} = \frac{v}{l}, \quad (187)$$

where v is the electron velocity and l the average grain size[104]. The parameters used in Eqs.(183, 185 and 186) are listed in Table 3.

The DOS in the conduction band for silicon nanowires with a length of 10 μm and various diameters is shown in Fig.34. The DOS profile of a narrow silicon nanowire (5 nm) is sharp, and this is due to strong quantum confinement. With diameter increases, DOS is getting smoother. The DOS profile of a nanowire with diameter of 30 nm is similar to that of 50 nm.

Assume all dopants are ionized at 300 K, the Fermi level in nanowire is determined

Figure 34: Electron density of states (DOS) in the conduction band ($E - E_c$) of Silicon nanowires with length $10 \mu\text{m}$ and various diameters (5 nm, 10 nm, 30 nm and 50 nm).

Figure 35: Fermi level relative to the bottom of the conduction band ($\mu - E_c$) in Silicon nanowires with the change of N-type doping concentration N at 300 K.

Figure 36: (a): The Seebeck coefficient S , (b): Electric conductivity σ , (c): Thermal conductivity by charge carriers κ_e , and (d): the relative error of Wiedemann-Franz law $(\kappa_{WF} - \kappa_e)/\kappa_e$ of Silicon nanowires with the change of N-type doping concentration N at 300 K.

by the following equation:

$$N = 2 \int_{E_c}^{\infty} f(\mu - E, T) \cdot D(E) dE, \quad (188)$$

where N is the N-type doping concentration. At a particular doping concentration, narrower nanowire has higher Fermi level. This is because the first energy level in conduction band is shifted up significantly in the presence of strong quantum confinement. With increase in doping concentration, Fermi level is shifting up (Fig.35), Seebeck coefficient is decreasing (Fig.36a), electric conductivity and thermal conductivity by charge carriers are increasing (Fig.36b-c). In this case, it is ambiguous as to the quality of the charge transport property to TE effect by using these three parameters.

The Wiedemann-Franz law, which states the relation between thermal conductivity by charge carriers and electric conductivity (Eq.(189)), is invalid[105] in the

presence of strong thermoelectric effect.

$$\kappa_{WF} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \sigma, \quad (189)$$

The relative error of Wiedemann-Franz law,

$$error = \frac{\kappa_{WF} - \kappa_e}{\kappa_e}, \quad (190)$$

is shown in Fig.36d. It is clear that, Wiedemann-Franz law is still valid in degenerate region (with high doping concentration). This is because thermoelectric effect is normally negligible in degenerate region, and the derivation of Wiedemann-Franz law needs to ignore thermoelectric field[37]. It is also important to notice, the error is significant in non-degenerate region, especially for narrow nanowires. Thus, to determine the thermal conductance by charge carriers of a TE device, one needs to go back to the original definition as given by Eq.(166).

The electronic TE efficiency ξ and the electronic equivalent thermal conductivity κ_P are shown in Fig.37. In degenerate region ($N > 10^{19} \text{ cm}^{-3}$), where Wiedemann-Franz law is valid, ξ is very small, this is consistent with the discussion above. In degenerate region, it is unlikely to have high FOM, as FOM is bounded by limit 1 (Eq.(178)). It is also hard to achieve high FOM when doping concentration is too low ($N < 10^{17} \text{ cm}^{-3}$). That is because, κ_P is small. To achieve high FOM, an extremely low κ_l is required, and that is difficult. The optimal region for FOM is where the Fermi statistics transit from non-degenerate to degenerate. For these silicon nanowires, the region is with the doping concentration change from 10^{17} cm^{-3} to 10^{19} cm^{-3} , as indicated by circle in Fig.37.

We choose doping concentration of 10^{18} cm^{-3} in the discussion of FOM with the change of κ_l (Fig.38). When κ_l is small enough, narrower nanowires with sharp DOS have higher FOM, and the FOM is bounded by limit 1, which is defined by ξ only. For large κ_l , FOM is approaching limit 2 and κ_l is the dominate parameter in FOM.

Figure 37: (a): Electronic thermoelectric efficiency ξ , and (b): Electronic equivalent thermal conductivity κ_p with the change of N-type doping concentration N at 300K. The circle indicates the optimal region for figure of merit, where the Fermi statistics transit from non-degenerate to degenerate.

Figure 38: Figure of merit ZT of Silicon nanowires with N-type doping concentration 10^{18} cm^{-3} at 300 K. The limit 1 and limit 2 are determined by Eq.(178) and Eq.(179), respectively.

Generally, for a good TE device, κ_l should be small, so ξ is essentially an important index to tell the quality of a TE device.

In Fig.38, the FOM of the Si nanowire with 10nm in diameter is smaller than that with 5nm, 30nm and 50nm. This non-monotonicity of FOM with the change of the diameter can be ascribed to the non-monotonicity of ξ as shown in Fig.37a. From Eq.(176), ξ can be rewritten as

$$\xi = 1 - \frac{[\text{stdev}(E - \mu)]^2}{\langle (E - \mu)^2 \rangle} \quad (191)$$

With the decrease in diameter, the profile of DOS transit from a smooth type to the type with sharp peaks. Due to the first sharp peaks in DOS for nanowire with smaller cross-sectional area, electrons are occupying relative lower energy level to the Fermi level, so the term $\langle (E - \mu)^2 \rangle$ in Eq.(191) become smaller. For the nanowire with 10 nm in diameter, electron transport is contributed by more than one DOS peaks, therefore the standard deviation is not small enough and ξ is then relative smaller. However, with the further decrease in the diameter to 5 nm, only the first DOS peak contributes significantly to electron transport, the standard deviation approaches zero and ξ is close to one. In this case, the PDF is close to the PDF of the best thermoelectric device, which is confined within a narrow region ΔE .

6.1.6 Conclusion

The development of high FOM TE device can proceed in two directions. One direction focused on phonon transport, the target is to reduce thermal conductivity by phonons. Another direction, which is discussed in this work, focused on charge transport. By engineering the charge transport properties of the TE device, high electronic thermoelectric efficiency and electronic equivalent thermal conductivity can be achieved. Anyway, to have FOM greater than one, the electronic thermoelectric efficiency has to be greater than 0.5.

6.2 *Scattering effect on thermoelectricity*

6.2.1 Introduction

In recent years, the concept of ballistic transport in nano-scaled device becomes important. However, electron scatterings still occurs for the sake of defects, grain boundaries, phonons, and charges in the device. Electron scatterings affect the transport properties, and further influence the thermoelectric effect of the device. A previous work has studied the effect of nano-particle scattering on thermoelectric power factor[106]. It is found that the electron concentration is usually higher in the sample with nano-particles, implying the Seebeck coefficient is usually not affected and conductivity is increased at the optimum of the power factor. This work is based on low nano-particle concentration, which can be considered in low scattering strength. Thus, strong scattering on thermoelectric effect is still an open question.

In this section, we employ the non-equilibrium Green's function to investigate the electron transport properties in nanowire with the presence of scatterings. Scattering points are inserted into the nanowire, and are modelled by using the concept of Büttiker probes[39]. The response of the device to an external field, which can be due to a temperature difference or a biased voltage, is discussed within a wide range of scattering strength. From that, the conclusion of the influence of electron scatterings on thermoelectric effect is drawn out.

6.2.2 Model

In the modelled system as shown by Fig.39, we considered a nanowire coupled by two contacts, which are functioning as thermal and electrical reservoirs. The wire is made of silicon; with the orientation [100] and square cross-sectional shape. The wire is chopped into many slices parallel to the contact interface with the thickness (a_z) equal to 0.3nm. The effective potential energy for the slice at the position z is given

Figure 39: The schematic of the modelled system: a nanowire coupled by two contacts at both ends, the scattering points denoted by the square box is coupled to Büttiker probe through a virtual contact.

by following expression.

$$E_{n_x, n_y}(z) = \frac{\hbar^2 \pi^2}{2} \left[\frac{1}{m_x^*} \left(\frac{n_x}{l_x} \right)^2 + \frac{1}{m_y^*} \left(\frac{n_y}{l_y} \right)^2 \right] + V(z) \quad (192)$$

The variables n_x, n_y are the quantum numbers for the energy in transverse direction; l_x, l_y are the side length of the cross-section and are set to 5 nm; $V(z)$ is the electrical potential energy; m^* the effective mass; and $\hbar$ the Dirac constant. The subscript of the effective potential energy (n_x, n_y) denotes a transverse mode. The Hamiltonian of the wire for such mode is constructed as follow:

$$H = \begin{bmatrix} E_{n_1, n_2}(1) + 2t_z & -t_z & 0 & \cdots \\ -t_z & E_{n_1, n_2}(2) + 2t_z & -t_z & \cdots \\ 0 & -t_z & \ddots & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \quad (193)$$

where t_z is the coupling energy between two slices with the expression $\hbar^2/(2m_z^*a_z^2)$, which is about 461 meV for this setup.

To reveal the effect of the electron scattering, the concept of Büttiker probes is introduced. Scattering points are inserted into the wire. For a scattering point, it is coupled to a Büttiker probe with the coupling strength (U), as shown in Fig.39, the scattering point is denoted by a square in the wire. The coupling strength determines the magnitude of the electron scatterings. For convenience, we define a scattering

factor α to represents the relative scattering strength to the coupling strength between two slices, i.e. $U = \alpha \cdot t_z$. To have an intuitive feel of the scattering strength, the thermal energy is about 26meV, which is equivalent to α equal to 0.056 at room temperature (300 K).

In this model, the Büttiker probes are essentially virtual contacts. Therefore, it is convenient to use an index i to label the entire contacts in the system, which includes the both virtual and real contacts. The self-energy due to the contact i is given by

$$\Sigma_i(E) = U^2 \cdot \frac{-e^{i \cdot k_i(E) \cdot a_z}}{t_z \cdot a_z}, \quad (194)$$

where $k_i(E)$ is the longitudinal wave vector and is determined by

$$k_i(E) = \sqrt{\frac{2m_z^*}{\hbar^2} [E - E_{n_1, n_2}(z)]}. \quad (195)$$

The formula for self-energy, Eq.(194), is generally for Büttiker probes with the coupling strength U . However, by setting α equal to one, the self-energies due to left or right contact can also be determined. The total self-energies of the wire is the sum of the contributions from each contact. Then, the broadening functions of contact i is obtained from its self-energy:

$$\Gamma_i(E) = -2 \text{Im}[\Sigma_i(E)]. \quad (196)$$

The retarded and advanced Green's function of the wire, G^R and G^A , are determined by the equations:

$$G^R(E) = [E + i\epsilon - H - \Sigma(E)]^{-1}, \quad (197)$$

$$G^A(E) = [G^R(E)]^\dagger, \quad (198)$$

where ϵ is a small positive number. With that, the electron transmission function between contact i and contact j is given by

$$T_{i,j}(E) = \text{Tr}[\Gamma_i G^R \Gamma_j G^A]. \quad (199)$$

The electrical current of contact i is then determined by the Landauer-Büttiker formula:

$$I_i = \frac{2e}{h} \int dE \sum_{j \neq i} T_{i,j} \cdot (f_i - f_j), \quad (200)$$

where the Fermi-Dirac distribution at contact i with the fermi level $E_{f,i}$ is defined as

$$f_i = [e^{\frac{E - E_{f,i}}{k_B T}} + 1]^{-1}. \quad (201)$$

To fulfill the charge conservation, the current of any Büttiker probe should be equal to zero. This condition is achieved by adjusting the Fermi level of the probe using the Jacobian method. The Fermi levels in the left and right contacts are determined by assuming that all donors are ionized, and the donor concentration used in the computation is 10^{18} cm^{-3} . The number of electrons in each slices are given by the diagonal elements of n , which is determined by the following expression:

$$n = \frac{1}{\pi} \int dE \sum_i f(E, E_{f,i}) G^R \Gamma_i G^A. \quad (202)$$

The potential energy $V(z)$ for each slice is then updated by Poisson's equation using the electron density determined by above formula. Therefore, a self-consistent iteration is carried out.

6.2.3 Discussion

In the following, the effect of scattering points is discussed with the absence of external field at first, followed by applying a voltage to the wire. In the last, the scattering effect to the Seebeck coefficient and power factor with a finite temperature difference across the wire is investigated. In these discussions, the wire is assumed to be at room temperature.

6.2.3.1 Trapping and Diffraction

In this subsection, the length of the nanowire is set to 18 nm, and two scattering points are inserted at the positions $z = 6 \text{ nm}$ and $z = 12 \text{ nm}$. With the absence of

external field, i.e. both temperatures and voltages in the two contacts are equal, the electron charge density along the wire is determined and shown in Fig.40, in which “SP1” and “SP2” denote the scattering points. When no scattering occurs in the wire ($\alpha = 0$), due to the scattering at the interfaces between wire and contacts, electrons are accumulated at both ends of the wire, that incur the repulsion of electron as the result of the Coulomb force. Therefore, a fluctuation of electron density is observed in the wire, as shown by the “Ballistic” curve in Fig.40a. When the scattering strength getting slightly stronger ($\alpha < 0.1$), the electron wave function in the wire is reconstructed due to the perturbation of the scattering point, but this effect is not significant. Electron scattering occurs when the electron collides with the scattering points, and electrons are accumulated in the wire. Fig.40a shows the stronger scattering strength, the more electrons are trapped inside the wire, especially near the scattering points in the weak scattering region ($\alpha < 0.1$). This result is consistent with the previous work[106]. However, in strong scattering region, this effect vanishes. This is because electrons prefer avoiding the scattering points than being scattered. This mechanism is the diffraction of electrons and is achieved by reconstructing the electron wave functions with a smaller probability near the scattering points. Therefore, the chance of electron scatterings decreases, electron density near scattering points is smaller as shown in Fig.40b.

6.2.3.2 Voltage biased

In the following, we discuss a 9 nm nanowire at room temperature with a biased voltage. A single scattering point is considered with its position located at the center of the wire. In the case of ballistic transport ($\alpha = 0$), due to the external field, electron density is tilting toward one end of the wire, which is shown in Fig.41a. With slightly increases in the scattering strength, more electrons are accumulated in the wire, especially near the scattering point. This is consistent with the above

Figure 40: The electron density in a nanowire with the length 18 nm, two scattering points are inserted at the $z = 6$ nm and $z = 12$ nm, (a) is for the weak scattering and (b) is for the strong scattering. α is the scattering strength.

Figure 41: A 9 nm nanowire with the presence of biased voltage ΔV , (a): the electron density, and (b): the electrical current in weak scattering condition; (c): the electron density, and (d): the electrical current in strong scattering condition. α is the scattering strength.

discussion. With the presence of external electric field, the increment in electron density is conducive to the electrical current as shown by Fig.41b. However, in strong scattering region, electrons are bypassing the scattering point by reconstructing their wave functions. This leads to the accumulation of electrons, which blocks current flow, near the contact interfaces (Fig.41c). So, decrease in electrical current is expected (see Fig.41d).

As shown by Fig.42, with different bias voltages, the profiles of the electrical current with the change of scattering strength are similar: a rise followed by a drop. Furthermore, it is interesting to notice the scattering strength at which the maximum current occurs, is increasing with the biased voltage. This phenomenon can be understood in the following way. The electrons accumulated near the contact interface, which blocks current, can be driven by a higher biased voltage, which has stronger power of accelerating electrons. Thus, these electrons contribute to the electric current. With sufficiently large scattering strength, the effect of electric current blocking

Figure 42: A 9nm nanowire with the presence of various biased voltages, the electrical current with the change of scattering strength α .

by the accumulated electrons is significant, therefore current decreases.

6.2.3.3 Thermoelectricity

To discuss the thermoelectric effect, a 9 nm nanowire under a temperature difference is considered. The temperature difference is split into half and applied on each end of the wire, i.e. $T_L = T + \Delta T/2$ and $T_R = T - \Delta T/2$. In general, thermoelectric effect is evaluated in the condition that the device is at open circuit. Therefore, the net current is zero. For this reason, to offset the current, which should be produced by the temperature difference, an electric field is then generated. The ratio of the voltage difference over the temperature difference between two ends of the wire gives the Seebeck coefficient. To determine the conductance of the wire in the presence of temperature difference, a testing current (a small current) is injected into the wire, which would result in the reconstruction of the electric field, and the conductance is obtained from the change of the voltage difference.

In the weak scattering region ($\alpha < 0.1$), Seebeck coefficient is smaller with stronger scattering. That is because, in this region, the electrical conductance increases as indicated in Fig.43b, and this is consistent with the discussion on the electrical current.

Figure 43: A 9nm nanowire with temperature difference ΔT , (a): Seebeck coefficient, and (b): electrical conductance in weak scattering condition; (c): Seebeck coefficient, and (d): electrical conductance in strong scattering condition. α is the scattering strength.

With a larger conductance, a smaller electric field is sufficient enough to offset the current, which should be produced by temperature difference. Similarly, in the strong scattering region, Seebeck coefficient increases as the result of the decrease in the electrical conductance, as shown in Fig.43c and Fig.43d.

It is also important to notice another phenomenon from Fig.43b, the conductance increases with the temperature difference at first, and starts to decrease after the critical temperature difference. Furthermore, the critical temperature difference is increasing with the scattering strength. This is because a larger temperature difference intends to inject more electrons into the wire, and stronger scattering strength has better ability of trapping electrons in the weak scattering region. Therefore, more electrons are contributing to the conductance. When the temperature difference is more than the critical value, more electrons are injected than the wire could hold. To fulfill the open circuit condition, the electrons trapped in the wire are redistributed and starts to limit the current, which result in the drop of conductance. Due to this

Figure 44: A 9nm nanowire with temperature difference ΔT , the thermoelectric power factor with the change of scattering strength α with (a): small temperature difference, and (b): large temperature difference.

effect on conductance, Seebeck coefficient decreases at first and start to increase after the critical value. In strong scattering region, the fluctuations in conductance and Seebeck coefficient are not as strong as that in weak scattering region. This is because the chance of electron being scattered is reduced by electron diffraction, number of electrons trapped in the wire is smaller than the case of weak scattering.

Fig.44 shows the thermoelectric power factors with the change of scattering strength. The power factor place it maximum value at about $\alpha = 0.1$, and it drops dramatically after that. Because, the power factor is a function of the conductance and Seebeck coefficient, the explanation of the change in power factor can be ascribed to the change in the two parameters. At the optimum power factor, when $\alpha = 0.1$, for the case of ΔT equals to 0 K, 20 K and 50 K, from Fig.43a, the Seebeck coefficient drops by 8%, 13% and 11%; from Fig.43b, the conductance increases by 25%, 57% and 35%. Therefore the power factor is increased by 6%, 18% and 7%. Due to the shifting of the critical temperature difference (which is discussed in previous paragraph), the power factor has the maximum enhancement when temperature difference at about 20 K.

6.2.4 Conclusion

Weak and strong scatterings affect electron transport in different ways. In the case of weak scattering, electron trapping increase the electron density, hereafter boost the conductance significantly. Although the increment in conductance would reduce the Seebeck coefficient slightly, the power factor still increases. In the case of strong scattering, electron diffraction causes the redistribution of electrons, accumulation of electron at the ends of the wire blocks current flow, hence the conductance is reduced significantly. Although the Seebeck coefficient increases slightly, the power factor still decreases.

6.3 *Field effect thermoelectric device*

A specific profile, a single sharp peak on one side of Fermi level, of charge transmission probability function facilitates ZT enhancement. In previous works, such a profile is achieved by abrupt change in electron density of states (DOS), either in nanostructure (i.e. thin film [3], nanowire [1, 8, 80, 76, 107, 108, 109], quantum dot [8, 98, 99, 100, 110] and molecular junctions [97, 111, 112, 113]) or due to the distortion [96, 114]. Here, we propose a field effect TE device with the aim of producing such profile by an external electric field, which provides an additional degree of freedom [115, 116] in adjusting electron transport.

6.3.1 Device Description

The schematic of the proposed device is shown in Fig.45a. Two metal parts function as thermal and electric reservoirs, and are connected by semiconductor layers with length l_y and thickness l_x . The semiconductor layers are thin enough that their internal potentials are influenced by gate voltages significantly. In semiconductors, certain parts near contact interfaces with length l_b are named *uncovered region*, and

Figure 45: (a): The schematic of proposed device: two metal parts are connected by semiconductor thin films, between which gates and dielectric layers are inserted. (b): Band diagram of n-type leg with positive gate voltage applied. Region A, B and C refer to metal, uncovered region and covered region.

the central parts are *covered region*. With positive gate voltage (V_g) applied on the n-type leg of the device, (as shown in Fig.45b,) conduction band (E_c) in covered region is shifted down, providing large DOS near Fermi level (E_f). Meanwhile, potential barriers formed in uncovered region block the electron transport below E_f . Hence, a sharp electron transmission near Fermi level is expected.

6.3.2 Simulation and discussion

For demonstration purpose, we considered Pt (metal) contact with $\text{Si}_{0.8}\text{Ge}_{0.2}$ (semiconductor). With the n-type doping concentration $N_d = 10^{18}\text{cm}^{-3}$, Fermi level in semiconductor is near to the bottom of conduction band at room temperature (300K). The geometry parameters l_x , l_y , l_z and l_b are set equal to 10 nm, 300 nm, 100 nm and 6 nm. The x-y plane is discretized with spacing $a = 1$ nm in the x direction and $b = 2$ nm in the y direction. The system is modeled by Poisson equation and

non-equilibrium Green's function (NEGF)[35]. The discretized Poisson equation is

$$\begin{aligned} & \frac{a}{b}(V_{m+1,n} - V_{m,n}) + \frac{a}{b}(V_{m-1,n} - V_{m,n}) + \frac{b}{a}(V_{m,n+1} - V_{m,n}) + \frac{b}{a}(V_{m,n-1} - V_{m,n}) \\ &= -\frac{ab}{\varepsilon}q(N_d - \rho)_{m,n}, \end{aligned} \quad (203)$$

where q is unit of charge, m and n are the indexes of discretized points in x or y directions. The dielectric constants ε are set to $12.6\varepsilon_0$ [117] and $3.9\varepsilon_0$, for semiconductor and dielectric layer, where ε_0 is the vacuum permittivity. Electron density ρ is determined by NEGF as follow. The Hamiltonian of discretized semiconductor is

$$\begin{aligned} H_{(m,n),(m,n)} &= 2t_x + 2t_y + E_z + V_{m,n}; \\ H_{(m\pm 1,n),(m,n)} &= -t_x; t_x = \hbar^2/(2m_t^*a^2); \\ H_{(m,n\pm 1),(m,n)} &= -t_y; t_y = \hbar^2/(2m_l^*b^2); \\ E_z &= (\hbar^2/2m_t^*)(n_z\pi/l_z)^2; n_z = 1, 2, 3, \dots, \end{aligned} \quad (204)$$

where $\hbar$ is reduced Planck constant. Electron effective masses in transverse and longitudinal directions are set equal to $m_t^* = 0.19m_e$ and $m_l^* = 0.92m_e$ [117] (, where m_e is free electron mass). By using electron gas approximation, the band edge in metal (E_{mc}) is 5.898 eV below Fermi level, determined from by following equation:

$$E_f - E_{mc} = \frac{\hbar^2}{2m_e}(3\pi^2n_a)^{\frac{2}{3}}, \quad (205)$$

where concentration of atoms (n_a) is equal to $6.513 \times 10^{28}\text{m}^{-3}$ for Pt. The self-energy due to metal contact (Σ) is then determined by:

$$\Sigma(E, m, m') = -\frac{(t_{y,m_e} + t_y)^2}{t_{y,m_e}} \left(\frac{a}{l_x}\right) \sum_{n_x, n_z} \frac{\sin(k_y b) \exp(ik_y b)}{k_y} \sin\left(\frac{n_x \pi}{l_x} x_m\right) \sin\left(\frac{n_x \pi}{l_x} x_{m'}\right); \quad (206)$$

$$t_{y,m_e} = \hbar^2/(2m_e b^2); \quad (207)$$

$$k_y = \sqrt{2m_e[E - (E_f - E_{mc} + E_x + E_z)]}. \quad (208)$$

Figure 46: The proposed device with $V_g = 0.08$ eV. (a): The electron transmission function. Electrons transmission below E_f are blocked by barriers. (b): Electron density of states are shifted to lower energy due to the positive gate voltage.

With retarded Green's function $G^R = (E - H - \Sigma)^{-1}$ and broadening function $\Gamma = -2\text{Im}(\Sigma)$, electron density is calculated by:

$$\rho = \frac{1}{\pi} \int G^R (\Gamma_L f_L + \Gamma_R f_R) (G^R)^\dagger dE, \quad (209)$$

and substituted to Eq.(203). Until the electric potential in semiconductor (V) is self-consistent in Eqs.(203 and 209), electron DOS and transmission function are obtained from NEGF:

$$DOS = -\text{Im}(G^R)/\pi; \quad (210)$$

$$T(E) = \text{Tr}[\Gamma_L G^R \Gamma_R (G^R)^\dagger]. \quad (211)$$

With $V_g = 0.08$ eV, the conduction band in $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film is shifted down below E_f (Fig.46b) and transmission below E_f is blocked (Fig.46a). This is exactly consistent with the original target of the proposed device. With $T(E)$, the electric conductance G , thermal conductance by electron K_e and Seebeck Coefficient S are determined by Eqs.(165, 166 and 167). The lattice thermal conductivity of $\text{Si}_{0.8}\text{Ge}_{0.2}$ is $6.28\text{W}/(\text{mK})$ [117].

Figure 47: Related parameters to TE effect at 300 K, with various gate voltages. (a): Figure of merit ZT ; (b) Thermal conductance by electron K_e ; (c) Electric conductance σ ; (d) Seebeck Coefficient S .

Fig.47 shows ZT , S , K_e and G of the device with the change of V_g . When V_g is increasing from 0 to 0.02 eV, barriers are forming, "peak A" in DOS (Fig.46b) starts contributing to electron transport, hence S increases. When V_g increases to 0.06 eV, "peak A" is shifted to lower energy, and results in the decrease of S . However, with the presence of a transmission peak above E_f , G increases faster than K_e (refer to Eqs.(165 and 166)), so ZT increases. When V_g become much larger, "peak A" is shifted below E_f , that weakens the transmission peak above E_f , thus ZT decreases until "peak B" in DOS (Fig.46b) starts contributing to electron transport at V_g equal to 0.1 eV. In the following range of V_g , ($0.1 < V_g < 0.2$), similar events happen to "peak B", except electron transport above E_f is enhanced significantly by larger V_g , which makes the potential barriers much thinner. When V_g equal to 0.16eV, ZT reach its maximum value of 16.13. When V_g is greater than 0.2 eV, barriers become so thin that electron tunneling below E_f contributes to electron transport largely. Hence, K_e increases much faster than G . Also, S decreases, so does ZT . When V_g is greater than 0.25 eV, "peak B" is no longer contributing to electron transport, thereby G and K_e decrease.

6.3.3 Conclusion

In conclusion, we propose an field effect thermoelectric device, which has two controllable parameters: gate voltage and length of uncovered section to adjust its electron transport properties. A simple theoretic model is developed to demonstrate the potential of the device in achieving high ZT . With the theoretic model, the device, $\text{Si}_{0.8}\text{Ge}_{0.2}$ thin film with Pt contacts, is capable to achieve ZT of 16.13.

CHAPTER VII

CONCLUSION

7.1 Perspectives

The object of the research is to characterize and understand the transport phenomenon when the device is shrunk down to Nano scale. This knowledge is useful to be turned into technology for the next generation devices.

7.1.1 Phonon transport

For the transistor device, one desire higher thermal conductance that is better for the heat dissipation for the semiconducting material. For the thermoelectric device, one desire lower thermal conductance to ensure the conversion efficiency. The development of either device requires the establishment of phonon engineering.

Phonon transport is sensible to the structural parameters of the device, like the surface effect, diameter of the wire in this study, therefore to control the shape and structure of the device is a challenging work in the fabrication. The structural parameters can be adjusted easily in the theoretical model; one could test different structural configurations to search for the desired phonon transport profile. Besides the structural parameter, phonon scattering induced by electron-phonon coupling and defects are the topics need to be further addressed. The influence of the Kohn anomaly in phonon band dispersion is an interesting topic for both electron and phonon transport.

Regarding the phonon model used in this project, there is a potential to improve the generation of the dynamical matrix. We used one of the simplest force field to determine the dynamical matrix. It is possible to use first principle calculation or the

force field with long distance coupling to determine it.

7.1.2 Electron transport

In the topic of electron transport, this project focused more on the thermoelectric device. It is clear that, the object is to improve the conversion efficiency which is indexed by the figure of merit. In thermoelectric device, electron transport is driven by the temperature difference, which is in term of the difference in the statistical distributions between the cold and hot end. When electron transports from one contact to another, it not only carry the charge but also the heat. That gives a limit to the figure of merit. Therefore, the investigation on the electron transport should focus on the spectrum transmission. It is likely electron tunnelling will be a method to select the “right” electron in the transport process.

There are a few possible further improvements for the electron transport model used in the project. Instead of the effective mass approach for the Hamiltonian, the atomistic tight binding model or the first principle method will give better precision for the electronic structure. The electron scattering in the transport model powered by Green’s function should be revisited. The model of inelastic scattering in Green’s function is urged.

7.2 Summary

In the project, “Investigation on transport properties in nanowires with contacts”, both phonon transport and electron transport in a two-probe system are studied. Methods including non-equilibrium Green’s function and Boltzmann transport theory are used in the investigation.

In phonon transport, the effect due to the surface reconstruction at the contacts’ surface is investigated at first. Lenard-Jones potential and bond-order-length-strength correlations are used in the setup of the dynamical matrix. The surface atomic bonds

are generally shorter and stronger with surface reconstruction. Due to this phenomenon, a blue shift in phonon DOS at contact surface is expected, and that enhances phonon transmission at high phonon frequency. Therefore, the thermal conductance contributed by phonon is weakened by surface reconstruction in low temperature region and enhanced in high temperature region.

Continue from the work mentioned above, the anharmonic effect in silicon atomic wire is considered. The anharmonic effect is due to the higher order term in the potential energy. The thermal conductance contributed by phonon is split into two terms: conductance due to harmonic phonon transport and conductance due to anharmonic phonon transport. Anharmonic effect enhances phonon scattering and reduces thermal conductance, especially in higher temperature regions. With the presence of surface reconstruction, the anharmonic effect becomes even stronger.

Not only silicon atomic wire, the phonon transport in silicon nanowire with square shaped cross-section area is also investigated. With the decrease of its cross-sectional area, the number of transverse phonon modes is reduced that limits phonon transmission, hence leads to a smaller thermal conductance density. Besides that, the thermal conductance of silicon nanowire becomes sensitive to the location of the Ge atom substitution. It is found that interior atom substitution has more impact on thermal conductance over surface atom; substitution near contact surface reduces thermal conductance significantly; thermal conductance is suffering a serious variation due to the random distribution of the substitution locations; 17% content of Ge in the nanowire is sufficient to reduce the thermal conductance by 80%.

To study the gold atomic wire, embedded atom method is used instead of Lennard-Jones potential. Buffer layers or neck regions are inserted between the wire and contacts. Also, the bond length and strength modification in atomic chain low-dimensional structure was taken into consideration by using bond-order-length-strength correlation premise. It is found that the contact interfaces between an atomic chain

and contact reservoir, i.e., neck region or buffer layers, play an important role in phonon transport. The more buffer layers the less thermal conductance.

To improve thermoelectric efficiency, the physical phenomenon of thermoelectric effect is re-visited. The important thermoelectric figure of merit is expressed in terms of powers, and it is mapped by two fundamental quantities. One is the electronic thermoelectric efficiency, which is purely determined by a probability distribution function of electron transport. Furthermore, electronic thermoelectric efficiency plays an important role in the upper limit of thermoelectric figure of merit, which is an important index to judge the quality of a thermoelectric device. For any thermoelectric device with figure of merit more than one, its electronic thermoelectric efficiency must be greater than 0.5. For demonstration purpose, the thermoelectric properties of silicon nanowire are investigated.

Besides that, the influence of electron scattering on thermoelectric effect is studied, and the scattering mechanism is modelled by using the concept of Büttiker probe. The effect of electron scattering is analysed under three conditions: without external field; with electrical field; and with temperature difference. It is found weak and strong scatterings affect electron transport in different ways. In the case of weak scattering, electron trapping increase the electron density, hereafter boost the conductance significantly. Although the increment in conductance would reduce the Seebeck coefficient slightly, the power factor still increases. In the case of strong scattering, electron diffraction causes the redistribution of electrons, accumulation of electron at the ends of the wire blocks current flow; hence the conductance is reduced significantly. Although the Seebeck coefficient increases slightly, the power factor still decreases. The power factor is enhanced by 6% – 18% at the optimum scattering strength.

APPENDIX A

PUBLICATION LIST

1. Jing Li, T. C. Au Yeung, C. H. Kam, Xuean Zhao, Qing-Hu Chen, Yue Peng, and Chang Q. Sun, The effect of surface bond reconstruction of thermal contact surfaces on phonon transport in atomic wire. *Journal of Applied Physics*, **106**, 054312 (2009), has been selected for the September 21, 2009 issue of *Virtual Journal of Nanoscale Science & Technology*.
2. Jing Li, T. C. Au Yeung, C. H. Kam, Yue Peng, Qing-hu Chen, Xuean Zhao, and Chang Q. Sun, Anharmonic phonon transport in atomic wire coupled by thermal contacts with surface bond reconstruction. *Journal of Applied Physics*, **106**, 014308 (2009).
3. Xuean Zhao, Jing Li, T. C. Au Yeung, C. H. Kam, Qing-Hu Chen, and Chang Q. Sun, Phonon transport in atomic chains coupled by thermal contacts: The role of buffer layer. *Journal of Applied Physics*, **107**, 094312 (2010).
4. Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, The upper limit of thermoelectric figure of merit: Importance of electronic thermoelectric efficiency, *J. Phys. D: Appl. Phys.* **45**, 085102, (2012).
5. Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, Phonon transport in nanowire with contacts: Size and doping. *Journal of Applied Physics*, **111**, 094308 (2012), has been selected for the May 21, 2012 issue of *Virtual Journal of Nanoscale Science & Technology*.
6. Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, Influence of electron

scatterings on thermoelectric effect, submitted to Journal of Applied Physics
(accepted).

REFERENCES

- [1] Allon I. Hochbaum, Renkun Chen, Raul Diaz Delgado, et.al., Nature **451**, 163 (2008).
- [2] Rowe, D.M. (Ed.): Handbook of Thermoelectrics, CRC press, Boca Raton (1995)
- [3] R. Venkatasubramanian et al., Nature **413**, 597 (2001).
- [4] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, Science **297**, 2229 (2002).
- [5] Kuei Fang Hsu, Sim Loo, Fu Guo, Wei Chen, Jeffrey S. Dyck, Ctirad Uher, Tim Hogan, E. K. Polychroniadis, and Mercouri G. Kanatzidis, Science **303**, 818 (2004).
- [6] Akram I. Boukai, Yuri Bunimovich, Jamil Tahir-Kheli, Jen-Kan Yu, William A. Goddard Iii, and James R. Heath, Nature **451**, 168 (2008).
- [7] Sebastian Volz, Ali Shakouri, and Mona Zebarjadi, in Thermal Nanosystems and Nanomaterials (Springer Berlin / Heidelberg, 2009), Vol. 118, pp. 225-299.
- [8] Natthapon Nakpathomkun, H. Q. Xu, and Heiner Linke, Phys. Rev. B **82**, 235428 (2010).
- [9] N.Mingo and Liu Yang, Phys. Rev. B **68**, 245406 (2003).
- [10] D. G. Cahill, W. K. Ford, K. E. Goodson, G. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, J. Appl. Phys. **93**, 793 (2003).
- [11] S. Lepri, R. Livi and A. Politi, Phys. Rep. **377**, 1 (2003).
- [12] B. Li, J. Wang, L. Wang, and G. Zhang, Chaos **15**, 015121 (2005).
- [13] Renkun Chen, Allon I.Hochbaum, Padraig Murphy, Joel Moore; Peidong Yang, and Arun Majumdar, PRL **101**, 105501 (2008).
- [14] Luis G. C. Rego, and George Kirczenow, PRL **81**, 232 (1998).
- [15] Takahiro Yamamoto, Satoshi Watanabe, and Kazuyuki Watanabe. **92**, 075502 (2004).
- [16] Dvira Segal, Abraham Nitzan, J. Chem. Phys. **117**, 3915 (2002).
- [17] Abhishek Dhar and Dibyenda Roy, J. Stat. Phys. **125**, 805 (2006).

- [18] R.T.Senger, S. Tongay, E. Durgun, and S. Ciraci, Phys. Rev. B **72**, 075419 (2005).
- [19] T.C. Au Yeung, M.X. Gu, Chang Q. Sun, George C.K. Chen, D.W.K. Wang, and V. Nosik, Phys. Rev. B **74**, 155317 (2006).
- [20] Jing Li, T. C. Au Yeung, C. H. Kam, Xuean Zhao, Qing-Hu Chen, Yue Peng and Chang Q. Sun, J. Appl. Phys, **106**, 054312(2009).
- [21] Jing Li, T. C. Au Yeung, C. H. Kam, Yue Peng, Qing-Hu Chen, Xuean Zhao and Chang Q. Sun, J. Appl. Phys, **106**, 014308(2009).
- [22] Xuean Zhao, Jing Li, T. C. Au Yeung, C. H. Kam, Qing-Hu Chen, and Chang Q. Sun, J. Appl. Phys, **107**, 094312 (2010).
- [23] Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, J. Phys. D: Appl. Phys. **45**, 085102, (2012).
- [24] Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, Influence of electron scatterings on thermoelectric effect, J. Appl. Phys (to be published) (2012).
- [25] Jing Li, Tin Cheung Au Yeung, and Chan Hin Kam, Phonon transport in silicon nanowire: size and doping, J. Appl. Phys, **111**, 094308 (2012).
- [26] The Feynman Lectures on physics Volume 1 39-9 (1963).
- [27] J.S.Blackmore, Solid State Physics, the Press Syndicate of the University of Cambridge, (1985).
- [28] K.A. Gschneidner, Solid State Physics, Vol. 16, (1964).
- [29] Albert Messiah, Quantum Mechanics, Chapter XII The Harmonic Oscillator, 432 (1999).
- [30] Joseph Callaway, Quantum Theory of the Solid State, Chapter 2, lattice Dynamics (1991).
- [31] Blencowe, M. P. , Phys. Rev. B **59**, 4992 (1999).
- [32] N.Mingo, Phys. Rev. B **74**, 125402 (2006).
- [33] Jian_Sheng Wang, Jian Wang, and Nan Zeng, Phys. Rev. B **74**, 033408 (2006).
- [34] Masahiro Morooka, Takahiro Yamamoto, and Kazuyuki Watanate, Phys. Rev. B **77**, 033412 (2008).
- [35] S. Datta, Electronic Transport in Mesoscopic Systems (Cambridge University Press, Cambridge, England, 1995).
- [36] Charles M. Wolfe, Nick Holonyak Jr., and Gregory E. Stillman, Physical Properties of Semiconductors (Prentice-Hall International, Inc.)

- [37] N. W. Ashcroft and N. D. Mermin, Solid State Physics (Saunders College Publishing, Orlando, FL, 1976).
- [38] Magnus Paulsson, <http://nanohub.org/resources/1932> (2006).
- [39] R. Venugopal, M. Paulsson, S. Goasguen, S. Datta, and M. S. Lundstrom, J. Appl. Phys. **93**, 5613 (2003).
- [40] C.Q. Sun, S. Li, and C.M. Li, J. Phys. chem. B **109**, 415 (2005).
- [41] C.Q. Sun, Prog. Solid State Chem **35**,1 (2007).
- [42] N.Mingo, Phys. Rev. B **68**, 113308 (2003).
- [43] Agrat, N. Yeyati, A. L. van Ruitenbeek, J. M. Phys. Rep., **81**, 377(2003).
- [44] T. S. Tighe, J. M. Worlock and M. L. Roukesb, Appl. Phys. Lett. **70** 2687(1997).
- [45] Yang Zhao, Chi-Chiu Ma, GuanHua Chen, and Qing Jiang, Phy. Rev. Lett. **91** 175504(2003).
- [46] S. Peláez, P. García-Mochales, and P. A. Serena, phys. stat. sol. (a) **203**, No. 6, 1248 (2006).
- [47] S. Peláez, P. A. Serena, surface Science **60** 4163(2007).
- [48] P. García-Mochales, R. Paredes, S. Peláez, and P. A. Serena, Nanotechnology **19** 225704(2008).
- [49] Hideaki Ohnishi, Yukihiro Kondo and Kunio Takayanagi, Nature **395** 780(1998).
- [50] A. I. Yanson, G. Rubio Bollinger, H. E. van den Brom, N. Agrait and J. M. van Ruitenbeek, Nature **395** 783(1998).
- [51] J. Bettini, F. Sato, P. Z. Coura, S. O. Dantas, D. S. Galva and D. Ugarte, Natue Nanotechnology **1** 182(2006).
- [52] Daniel Sánchez-Portal, Emilio Artacho, Javier Junquera, Pablo Ordejón, Alberto Garc, and José M. Soler, Phys. Rev. Lett. **83**, 3884(1999).
- [53] Sune R. Bahn and Karsten W. Jacobsen, Phys. Rev. Lett. **87** 266101(2001).
- [54] W. Zhang, T. S. Fisher and N. Mingo, J. Heat Trans., Part B, **51** 333(2007).
- [55] Takahire Yamamoto and Kazuyuki Watanabe, Phys. Rev. Lett. **96** 255503(2006).
- [56] Jian-Sheng Wang, Nan Zeng, Jian Wang, and Chee Kwan Gan, Phys. Rev. E, **75** 061128(2007).

- [57] W. Zhang, N. Mingo and T. S. Fisher, Phys. Rev. B, **76** 195429(2007).
- [58] Tokushi Kizuka, Phys. Rev. B, **77**, 155401(2008).
- [59] Murray S. Daw and M. I. Baskes, Phys. Rev. B **29** 6443(1984).
- [60] J. S. Nelson, Erik C. Sowa, and Murray S. Daw, Phys. Rev. Lett., **61** 1977(1988).
- [61] J. Cai and Y. Y. Ye, Phys. Rev. B, **54** 8398(1996).
- [62] James H. Rose, John R. Smith, Francisco Guinea and John Ferrante, Phys. Rev. B **29** 2963(1984).
- [63] R. A. Johnson, Phys. Rev. B, **37** 9324(1988).
- [64] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B, **33** 7983(1986).
- [65] F. Guinea, C. Tejedor, F. Flores, and E. Louis, Phys. Rev. B **28** 4397(1983).
- [66] Chang Q. Sun, C. M. Li, S. Li, and B. K. Tay, Phys. Rev. B, **69** 245402(2004).
- [67] Chang Q. Sun, Phys. Rev. B, **69** 045105(2004).
- [68] G. D. Mahan, *Many-particle Physics* (Plenum, New York, 2000).
- [69] J. W. Lynn, H. G. Smith, and R. M. Nicklow, Phys. Rev. B, **8** 3493(1973).
- [70] G. Gilat and L. J. Raubenheimer, Phys. Rev. **144** 390(1966).
- [71] Deyu Li, Yiyang Wu, Philip Kim, Li Shi, Peidong Yang, and Arun Majumdar, Appl. Phys. Lett. **83** 2934(2003).
- [72] M. N. Ou, T. J. Yang, S. R. Harutyunyan, Y. Y. Chen, C. D. Chen, and S. J. Lai, Appl. Phys. Lett. **92** 063101(2008).
- [73] Olivier Bourgeois, Thierry Fournier, and Jacques Chaussy, J. Appl. Phys. **101**, 016104(2007).
- [74] Luis G. C. Rego and George Kirczenow, Phys. Rev. Lett. **81** 232(1998).
- [75] K. Schwab, E. A. Henriksen, J. M. Worlock and M. L. Roukes, Nature **404** 974(2000).
- [76] Troels Markussen, Antti-Pekka Jauho, and Mads Brandbyge: Phys. Rev. Lett. **103**, 055502 (2009).
- [77] Davide Donadio and Giulia Galli: Phys. Rev. Lett. **102**, 195901 (2009).
- [78] Pierre Martin, Zlatan Aksamija, Eric Pop, and Umberto Ravaioli: Phys. Rev. Lett. **102**, 125503 (2009).

- [79] Renkun Chen, Allon I. Hochbaum, Padraig Murphy, Joel Moore, Peidong Yang, and Arun Majumdar: Phys. Rev. Lett. **101**, 105501 (2008).
- [80] Jie Chen, Gang Zhang, and Baowen Li: Nano Lett. **10**, 3978 (2010).
- [81] Lihong Shi, Donglai Yao, Gang Zhang, and Baowen Li: Appl. Phys. Lett. **96**, 173108 (2010).
- [82] W. Zhang, T. S. Fisher, and N. Mingo: J. Heat Transfer **129**, 483 (2007).
- [83] J. Garg et al., Phys. Rev. Lett. **106**, 045901 (2011).
- [84] W.A. Harrison, Electronic Structure and the Properties of Solids (Dover, New York, 1989).
- [85] W. Zhang, N. Mingo, and T. S. Fisher: Phys. Rev. B **76**, 195429 (2007).
- [86] Y. S. Ju and K. E. Goodson, Appl. Phys. Lett. **74**, 3005 (1999).
- [87] P. G. Sverdrup, Y. S. Ju and K. E. Goodson, ASME J.Heat Transfer **123**, 130 (2001).
- [88] Francis J. DiSalvo, Science **285**, 703 (1999).
- [89] M.S. Dresselhaus G. Chen, G. Dresselhaus, J.-P. Fleurial and T. Caillat, Inter. Materials Rev. **48**, 45 (2003).
- [90] Keivan Esfarjani, Mona Zebarjadi, and Yoshiyuki Kawazoe, Phys. Rev. B **73**, 085406 (2006).
- [91] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A **93**, 7436 (1996).
- [92] Xiaofeng Fan, Gehong Zeng, Chris LaBounty, et.al., Appl. Phys. Lett. **78**, 1580 (2001).
- [93] Ali Shakouri, Chris LaBounty, Joachim Piprek, Patrick Abraham, and John E. Bowers, Appl. Phys. Lett. **74**, 88 (1999).
- [94] Chris LaBounty, Ali Shakouri, and John E. Bowers, J. Appl. Phys. **89**, 4059 (2001).
- [95] S. Wang and N. Mingo, Phys. Rev. B **79**, 115316 (2009).
- [96] A. Popescu and L. M. Woods, Appl. Phys. Lett. **97**, 052102 (2010).
- [97] C. M. Finch, V. M. García-Suárez, and C. J. Lambert, Phys. Rev. B **79**, 033405 (2009).
- [98] Jie Liu, Qing-feng Sun, and X. C. Xie, Phys. Rev. B **81**, 245323 (2010).
- [99] Jun Zhou and Ronggui Yang, Phys. Rev. B **82**, 075324 (2010).

- [100] M. Tsaousidou and G. P. Triberis, J. Phys.: Condens. Matter **22**, 355304 (2010).
- [101] D. L. Rode and S. Knight, Phys. Rev. B **3**, 2534 (1971).
- [102] Yu. I. Ravich, B. A. Efimova, and V. I. Tamarchenko, Phys. Status Solidi B **43**, 11 (1971).
- [103] A. J. Minnich, H. Lee, X. W. Wang, G. Joshi, M. S. Dresselhaus, Z. F. Ren, G. Chen, and D. Vashaee, Phys. Rev. B **80**, 155327 (2009).
- [104] Chandan Bera, M. Soulier, C. Navone, Guilhem Roux, J. Simon, S. Volz and Natalio Mingo, J. Appl Phys. **108**, 124306 (2010).
- [105] T. E. Humphrey and H. Linke, Phys. Rev. Lett. **94**, 096601 (2005).
- [106] Mona Zebarjadi, Keivan Esfarjani, Ali Shakouri, et.al., Appl. Phys. Lett. **94**, 202105 (2009).
- [107] Z. Wu, J. B. Neaton, and J. C. Grossman, Physical Review Letters **100**, 246804 (2008).
- [108] H. J. Ryu et al., Phys. Rev. Lett. **105**, 256601 (2010).
- [109] L. Shi et al., Appl. Phys. Lett. **95**, 063102 (2009).
- [110] V. M. Fomin, and P. Kratzer, Phys. Rev. B **82**, 45318 (2010).
- [111] Y. Dubi, and M. Di Ventra, Rev. of Modern Phys. **83**, 131 (2011).
- [112] M. Paulsson, and S. Datta, Phys. Rev. B **67**, 241403 (2003).
- [113] M. Leijnse, M. R. Wegewijs, and K. Flensberg, Phys. Rev. B **82**, 045412 (2010).
- [114] J. P. Heremans et al., Science **321**, 554 (2008).
- [115] V. Sandomirsky et al., J. Appl. Phys. **90**, 2370 (2001).
- [116] I. Bejenari, V. Kantser, and A. A. Balandin, Phys. Rev. B **81**, 075316 (2010).
- [117] Schaffler F., in Properties of Advanced Semiconductor Materials GaN, AlN, InN, BN, SiC, SiGe . Eds. Levinshtein M.E., Rumyantsev S.L., Shur M.S., John Wiley & Sons, Inc., New York, 2001, 149-188.