Thermal properties of two-dimensional nanomaterials

Liu, Bo

2015

Liu, B. (2015). Thermal properties of two-dimensional nanomaterials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65403>

<https://doi.org/10.32657/10356/65403>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**THERMAL PROPERTIES OF TWO-DIMENSIONAL
NANOMATERIALS**

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LIU BO

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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ENGINEERING**

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

2015

Acknowledgements

I would like to express my sincere gratitude and appreciation to my supervisor Assistant Professor Zhou Kun for his guidance, support, patience and encouragement during my PhD study. This research would not have been possible without his instructive advice and help. I have immensely benefitted from his strict training on both scientific thinking and writing. His dedication and enthusiasm for research has been exemplary and motivating. His rigorous and serious attitude towards scientific research has deeply impressed me.

I also owe a great debt of gratitude to my co-supervisor Dr. Chilla Damodar Reddy for his inspiration and assistance in accessing essential information and knowledge that contributed to the success of this research work.

I gratefully acknowledge the Nanyang Technological University for providing the research scholarship and its High Performance Computing Center for computational support.

My appreciation also goes to Professor Sergey V. Dmitriev, Professor Jiang Jingwu and Dr. Julia A. Baimova. The discussions with them have been fruitful and helpful.

I would also like to thank all my group members and friends for their accompany and support during my PhD life.

Last but not least, I would like to express my heartfelt gratefulness to my mother for her continuous support and understanding and to my wife for her accompany and encouragement that really mean a lot to me.

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Abstract

Two-dimensional (2D) nanomaterials have attracted intensive interest in the past decades owing to their superior properties and prospective applications in nanodevices. Recently, there is an increasing demand for understanding the thermal properties of these nanomaterials. This demand is driven by the fact that thermal dissipation at the nanoscale has become a crucial issue because of the ever continuing miniaturization of nanodevices. In addition, thermal transport in nanomaterials has revealed many unique phenomena, of which the understanding would lead to novel nanotechnologies in thermal management. Most of these unique phenomena are related to an important characteristic of nanomaterial: their properties highly depend on their atomic structures which are often inevitably altered by chemical functionalization, strain and presence of structural interruptions induced during fabrication or application. Hence, this PhD study has been devoted to studying the thermal properties of 2D nanomaterials and understanding the structural alteration effects through the method of non-equilibrium molecular dynamics simulation. Three representative types of such 2D nanomaterials, namely, graphene (GE), silicene (SE) and MoS_2 have been investigated.

As one of the important chemical functionalization methods, hydrogenation has been widely used to tune the properties of nanomaterials and obtain their derivative counterparts. The simulation results have revealed that the thermal conductivity of hydrogenated GE is much lower than that of pristine GE and highly depends on both the hydrogen coverage and hydrogenation pattern. The two distinct mechanisms of phonon-interface and phonon-phonon scatterings were identified to be responsible for the low

thermal conductivity of hydrogenated GE. Similar to hydrogenation, isotopic doping was also found to play an important role in reducing the thermal conductivity of SE, an analogy of GE but in terms of silicon atoms. For the random doping pattern, the thermal conductivity of SE decreases nonmonotonically with the doping fraction and a maximum reduction of ~20% was obtained at the fraction of 50%. This reduction can be further enlarged if the doping atoms are arranged in a periodic pattern (superlattice structure) with the period smaller than 10 nm, especially when the periodic interfaces are roughened.

When the individual GE and SE were combined to form a hybrid GE/SE monolayer heterostructure, the GE/SE interface was identified as the main thermal resistance for the thermal transport. The effects of the temperature, monolayer length, interface mismatch strain and heat flux magnitude on the interface thermal conductance were systematically studied. A new mechanism of low-frequency kinetic waves was discovered to provide an additional channel for heat conduction in the GE/SE monolayer. Moreover, due to the intensive phonon spectrum mismatch between GE and SE, the thermal rectification effect was observed at their interface. When GE and SE were stacked together to form a hybrid GE/SE bilayer heterostructure, a low interface thermal conductance was obtained, which however could be enhanced by increasing the temperature and the interface coupling strength. Its interface thermal conductance could also be enhanced by the hydrogenation of its GE in an optimal pattern. Furthermore, the thermal rectification effect was observed at the bilayer interface, but its underlying mechanism was different from that for the monolayer interface.

The in-plane and out-of-plane thermal transport behaviors of a practically realized GE-based composite material, the GE/MoS₂ bilayer heterostructure, have been studied. It

was revealed that the in-plane thermal conductivity of the GE/MoS₂ bilayer can be well approximated by that of the GE monolayer through a simple linear relationship. Moreover, enhancing the interface coupling strength of this bilayer structure can efficiently improve its out-of-plane interface thermal transport while have a negligible effect on its in-plane thermal conductivity.

This PhD dissertation has investigated the unique thermal properties and behaviors of 2D nanomaterials and explained their underling mechanisms. This study will not only help to understand the heat dissipation and management of 2D nanodevices and thus to improve their functional performance, but also contribute to the development of next-generation nanotechnology for thermal applications.

List of Publications

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Chapter 1. Introduction

Two-dimensional (2D) nanomaterials have attracted tremendous attentions in the past decades because of their promising properties. The explosive studies of 2D nanomaterials have sparked intensive interest towards their applications in novel nanodevices with unique functionalities. The realization of these nanodevices has led to an increasing demand for understanding the thermal properties of 2D nanomaterials. In this chapter, a brief introduction is first conducted on 2D nanomaterials. Afterwards, the motivations and objectives for the study of the thermal properties of 2D nanomaterials are illustrated. Finally, the organization of the whole dissertation is presented.

1.1. Background

Low-dimensional nanomaterials are attracting tremendous interest in the past decades because of their anisotropic and dimension-tunable properties, as well as for their potential applications in next generation nanoelectronics with new functions beyond those possible with conventional Si and compound semiconductors. The 2D nanomaterials, characterized by a thickness in the order of nanometers, stand out from various other low-dimensional structures and have become one of the most important materials in nanotechnology. For example, the ultra-high surface area of these 2D nanomaterials makes them promising candidates for novel gas and energy storage devices. Meanwhile, 2D nanomaterials bridge the gap between one-dimensional (1D) nanomaterials and three-dimensional (3D) macroscopic bulk materials and open new basic problems of low-dimensional materials whose solutions can result in many new applications. As a result, in

the past decade great attentions have been paid to 2D nanomaterials, partially motivated by the successful preparation of free-standing graphene (GE) [1], the first 2D atomic crystal available.

Due to the novel and supreme physical and mechanical properties of GE, it has become the subject of intensive researches [1-15] ever since its successful fabrication from graphite via mechanical exfoliation method in 2004 [1]. The success in GE and its wide prospects have sparked broad interest towards searching new 2D GE-analogous nanomaterials. So far, various types of such nanomaterials have been discovered and synthesized, including silicene (SE) [16-21] and MoS_2 [22-27], each of which possesses unique properties and has great potentials in future nanotechnologies. The rapid development of the synthesis and processing of these 2D nanomaterials has led to the demand for a greater scientific understanding of their thermal properties. This demand is mainly driven by the following reasons.

Firstly, the continuous miniaturization and ever-increasing components density of the electronic devices place ever-increasing thermal loads on them. Following the Moore's law, the sizes of individual electronic device components reduce exponentially every year. The field-effect-transistors, one important component in most electronics, are now approaching a channel length of 100 nm and a 50-nm channel length has been projected for the near future. At the nanoscale, heat removal of the electronic devices is crucial for their reliability and performance, and thus the thermal design has become one integral part in their development. Moreover, as the electronic devices approach the nanoscale, their thermal transports demonstrate features that are dramatically distinct from those observed

at the macroscale. These unique features should also be well understood and incorporated into the complete electrical-thermal designs of the electronic devices.

Secondly, the increasing usage and demand of the energy sources of our planet calls for practical and efficient solutions that provide novel and efficient ways of energy generation, consumption and recycling. An attractive solution is to utilize the newly developed nanotechnologies and nanomaterials to enhance the heat management. In some cases, such as the nanoscale electronics, nanomaterials with high thermal conductivities are needed to make thermal dissipation as efficient as possible. In other cases, such as the thermoelectric devices and thermal barrier coatings, nanomaterials or nanoparticles with low thermal conductivities are desired to improve the thermal conversion or preservation.

Thirdly, the understanding of thermal properties of nanomaterials can also lead to the establishment of novel nanotechnologies. Traditionally, phonons are considered as the main heat carriers as the electrons are the main electricity carriers. Recently, it has been found that the phonons can also be manipulated to carry and process information [28]. More importantly, various types of thermal logic devices have been theoretically proposed or even experimentally fabricated, such as thermal rectifier [29, 30], thermal transistor [31], thermal logic gate [32] and thermal memory cell [33]. Based on these basic thermal components, it is possible to construct thermal circuits similar to their electronic counterparts. The key mechanism that lies in these thermal components is the thermal rectification effect which describes that the heat transport is highly dependent on the temperature gradient direction, just like the effect in an electronic rectifier where the electrical gradient direction determines the electric transport. As compared to bulk materials, nanomaterials, especially some nanocomposites, show apparent thermal

rectification effect and have large rectifying ratios, and thus are more promising for the applications in thermal devices.

1.2. Motivations

The thermal properties of 2D nanomaterials root in their atomic structures and are much different from those of bulk materials. However, during the fabrication of 2D nanomaterials, the formation of structural defects such as voids, grain boundaries and dislocations are inevitable. The thermal transport properties of 2D nanomaterials are very sensitive to the presence and concentration of such defects, making it important that such effects should be understood.

Meanwhile, for each specific application of 2D nanomaterials, different approaches are applied to tune their properties. For instance, to apply GE as a semiconductor and replace currently widely used Si-based electronic devices, it is necessary to open the band gap of GE and transform it from a semi-metal to a semiconductor, via methods including chemical functionalization [34, 35], strain engineering [36] and defect engineering [37]. The employment of the functional groups and strain during the applications of 2D nanomaterials would dramatically change their structures and thus their thermal properties, which need to be explored for future development of nanotechnologies.

Furthermore, in 2D nanomaterial-based composites, the interfaces play a significant role in the overall thermal transport properties. This is because the presence of an interface severely disrupts the regular crystalline lattice of the 2D nanomaterial and usually produces a large interface thermal resistance. So far, most of the previous studies have focused on the electrical and optical properties of these 2D nanomaterial-based

composites, and their thermal properties have not been well explored, which thus becomes another motivation of this PhD study.

Due to the rapid development in computer science and technology, atomistic models have reached a level of accuracy that can often be compared with that of experimental results. Thus, atomic simulations are more frequently conducted now in the studies of nanomaterials. Nanoscale objects, such as GE, are usually modeled using either first-principles simulation or molecular dynamics (MD) simulation. Compared to the first-principles simulation, the MD simulation allows the system size to go relatively large, which facilitates the study of the thermal properties of nanomaterials.

1.3. Objectives

This proposed research would investigate the thermal properties of 2D nanomaterials via MD simulation. Three presentative materials (GE, SE and MoS₂) are selected for the investigation. Specifically, the main objectives are set as follows:

- Investigate the thermal properties of individual GE, SE and MoS₂, including the thermal conductivity, vibration modes, phonon spectrum and morphology;
- Study the effects of chemical functionalization, isotopic doping and strain on the thermal properties and understand the underlying mechanisms;
- Investigate the thermal transport behaviors at the interfaces of nanocomposites formed by GE, SE and MoS₂, as well as the influencing factors including the interface atomic structure, temperature and interface coupling strength;
- Provide guidance for efficient control and improvement of the thermal properties of 2D nanomaterials and explore their potential applications for next-generation

nanotechnology.

1.4. Dissertation outline

This PhD dissertation contains eight chapters. Following this introduction chapter, a comprehensive review on the three presentative 2D nanomaterials (GE, SE and MoS₂), the fundamentals of nanoscale thermal transport and MD simulation is given in Chapter 2. Chapter 3 presents the study of the thermal conductivity of hybrid hydrogenated GE sheets. Chapter 4 investigates the thermal conductivity of SE and the effect of isotopic doping. Chapter 5 focuses on the interface thermal conductance and rectification in hybrid GE/SE monolayers. Chapter 6 deals with the interfacial thermal conductance of SE/GE bilayer heterostructures and the effect of hydrogenation. Chapter 7 is concerned about the thermal transport in GE/MoS₂ bilayer heterostructures. Finally, conclusions are drawn and future works are recommended in Chapter 8.

Chapter 2. Literature Review

Different from that of bulk materials, the thermal transport in nanomaterials and nanostructures present novel physics and features that are not captured at the macroscale, such as the size dependence and the intensive phonon surface/edge scatterings. Moreover, as the systems are scaled down to the nanometer sizes, the interfaces and the structural distortions caused by defects, strain and functional groups start to play an important role in the thermal properties. The investigation of nanoscale thermal transport, particularly with the effect of structural distortions being taken into account, is still beyond the capabilities of experimental approaches due to the difficulties in measuring the temperature and heat flux. MD simulation, on the other hand, is capable of predicting the thermal properties of nanomaterials and studying the effect of various types of structure distortions by comprehensively analyzing the kinetic behaviors and interactions of the individual atoms. In this chapter, the atomic structures and properties of three representative 2D nanomaterials are first introduced. The characteristics of thermal transport at the nanoscale are then reviewed and the simulation approaches that have been adopted to study the nanoscale thermal transport are also discussed with special attentions given to the MD simulation approach and its fundamentals.

2.1. 2D nanomaterials and nanocomposites

In this PhD study, three types of 2D nanomaterials GE, SE and MoS₂ are considered for investigation. These materials are selected for the following fact: GE is the most promising 2D nanomaterial and has first been successfully synthesized in the free-

standing state; SE is the most GE-analogous nanomaterials reported since the discovery of GE and has the natural compatibility with the current Si-based semiconductor devices; MoS₂ stands for the most promising GE-analogous nanomaterials that can be obtained from the vast bulk transition-metal dichalcogenides. With the fast development in synthesis of 2D nanomaterials and the increasing understanding of their properties, different types of 2D nanomaterials are integrated to form composites for improved and predesigned functionalities and performances. In this section, the detailed atomic structures and properties of the three representative 2D nanomaterials as well as the GE-based nanocomposites are introduced.

2.1.1. GE

GE is a single layer of graphite with all carbon atoms arranged in a honeycomb lattice, as shown in Fig. 2.1. Intrinsic GE is a semi-metal or zero-gap semiconductor and the electrons and holes in GE can behave like zero-mass Dirac Fermions [1]. Experimental results from transport measurements show that GE has remarkably high electron mobility at room temperature, with the reported values in excess of $15000 \text{ cm}^2 \cdot \text{V}^{-1} \text{ s}^{-1}$ [2]. Both theoretical and experimental studies have revealed that single-layer GE has ultra-high thermal conductivities of about $3000\text{-}5000 \text{ W m}^{-1} \text{ K}^{-1}$ [3, 4]. Moreover, GE appears to be one of the strongest materials ever tested. Measurements have shown that GE has the intrinsic strength of 130GPa and the tensile modulus (stiffness) of 1 TPa which is 200 times greater than steel [5]. Some other excellent properties of GE have also been reported, including high transparency to white light [6], complete impermeability to any gases [7],

capability to sustain extremely high electric current [8], and high feasibility to be chemically functionalized [9, 10].

Fig. 2.1. Atomistic configuration of GE.

These supreme properties make GE promising in replacing many other materials in the existing applications and enhancing their performances. Moreover, the combination of these properties would also give rise to many novel technologies. As stated by the Nobel laureate Novoselov and his co-authors, “the combination of transparency, conductivity and elasticity will find use in flexible electronics; whereas transparency, impermeability and conductivity will find application in transparent protective coatings and barrier films; and the list of such combination is continuously growing”[11]. Thanks to the rapid development in GE production techniques, the laboratory procedures capable of obtaining high-quality and large scale GE are relatively simple and cheap now. It is believed that in the near future, GE will be developed for wide applications such as GE-based electronics [2, 12], optics[12], spintronics [13], hydrogen storage [9] and composite materials [14, 15], to name a few.

2.1.2. SE

Previous studies have demonstrated that many of the superb properties of GE can be attributed to its 2D honeycomb structure [2, 12]. The fact that Si lies in the same column of the periodic table with C has therefore evoked considerable attempts to produce a counterpart of GE in terms of Si, namely, SE. Specifically, SE can be regarded as an extreme case of doped GE, i.e., all the C atoms are replaced with Si atoms. Excitingly, SE has recently been synthesized in the form of nanoribbons on the Ag (001) and (110) surfaces, respectively [16]. Following this effort, Vogt *et al.* successfully synthesized large area Si monolayer on the Ag (1 1 1) surface [17], paving the way for the realization of free-standing SE sheets. Similar to GE, SE is also composed of hexagonal rings and exhibits remarkable electronic and magnetic properties according to first-principles calculations [18]. Moreover, SE is also a gapless semimetal and its charge carriers also behave as zero-mass Dirac Fermions with an ultra-high Fermi velocity of $\sim 1.3 \times 10^6$ m/s which is comparable to that found for GE [17, 19]. The GE-like Dirac cones have also been observed in SE [18].

Due to the similarity of SE and GE in their electronic properties, all the expectations of GE, such as high-speed nanoelectronic devices based on ballistic electron transport, can also be realized by SE. Meanwhile, the intrinsic compatibility of SE with the widely used Si-based semiconductors might make it more favorable than GE for future nanoelectronic devices. Furthermore, the electronic properties of SE can be tuned by applying external electric field, a method that is not applicable for GE [20, 21]. This characteristic makes SE a more suitable candidate for field effect transistor devices.

2.1.3. MoS₂

Besides SE, special attentions have also been attracted to another class of GE-analogous 2D nanomaterials obtained mainly from bulk transition-metal dichalcogenides (TMDs). TMD materials have layered structures in which layers stack upon each other and hold together by weak van der Waals interactions. Due to the weak interlayer interactions, isolated monolayers of TMDs can be cleaved along the layer plane as realized in the case of graphite.

Among the large variety of layered TMDs, MoS₂ is one of the most widely studied materials in recent years. Similar to GE, MoS₂ also has a hexagonal crystal structure, i.e., each Mo atom is six-fold coordinated, hexagonally packed between two three-fold coordinated S atoms [22], as shown in Fig. 2.2. Bulk MoS₂ is an indirect band-gap semiconductor with the band gap of 1.29 eV. However, a monolayer of MoS₂ transforms to a direct band-gap semiconductor with the band gap of 1.8 eV and shows a strong photoluminescence effect [23]. Moreover, the band gap can be further modified through the application of mechanical strain [24], electric field [25], surface adaption [26] and defects [27]. The presence of a direct band gap makes monolayer MoS₂ promising for integration of MoS₂-based microelectronics into photoelectronics that allow for efficient phonon-electron energy conversion. More importantly, the direct band gap of monolayer MoS₂ overcomes the drawbacks of gapless GE, which makes MoS₂ an essential complement to GE in the field of semiconducting applications.

Fig. 2.2. Atomistic configuration of monolayer MoS₂: (a) top view and (b) front view.

In addition to its unique electronic properties, monolayer MoS₂ also possesses good mechanical strengths. For example, the estimated in-plane stiffness ($180 \pm 60 \text{ Nm}^{-1}$) and effective Young's Modulus ($270 \pm 100 \text{ GPa}$) for monolayer MoS₂ were found to be close to those of steel [38]. The excellent mechanical properties of monolayer MoS₂ make it attractive as reinforcing components in composites or for the fabrication of flexible electronics.

2.1.4. GE-based nanocomposites

With the development of versatile and reliable synthetic routes to prepare GE, ranging from the bottom-up epitaxial growth to the top-down exfoliation of graphite, it is desirable to harness the promising properties of GE into composites through combining GE with different kinds of functional materials or GE-analogous nanomaterials. So far, GE-based composites have been successfully fabricated with inorganic nanostructures, organic crystals, polymers, biomaterials and carbon nanotubes (CNTs). These composites

are intensively explored for the applications of batteries, fuel cells, supercapacitors, photovoltaic devices and so on.

One interesting class of GE-based composites falls in the nanoscale region and is characterized by hybrid monolayer or hybrid multilayer heterostructures that contain GE nanoflakes or nanosheets. In such GE-based composites, GE is combined with other 2D nanomaterials through various types of interactions, such as strong covalent bonds, weak van der Waals forces or both.

A good example of GE-based heterostructures would be the GE/*h*-BN hybrid monolayers [39] and multilayers [40, 41], both of which have been successfully synthesized. In the hybrid GE/*h*-BN monolayer, the GE and *h*-BN flakes are combined with strong covalent bonds (Fig. 2.3). Due to their similar lattice structures and lattice constants, GE and *h*-BN match well in their hybrid monolayers and keep structurally stable.

Fig. 2.3. Atomistic model of a hybrid GE/*h*-BN monolayer with the *h*-BN nanoflakes embedded in a GE nanosheet [39].

Moreover, the fractions and distribution patterns of GE and *h*-BN flakes can be well controlled, bringing about unique structural features and physical properties that are not found in pure GE or *h*-BN monolayers [39]. Inspired by the hybrid GE/*h*-BN monolayer, other hybrid GE-based monolayers, such as GE/SE hybrid monolayer [42], have also been experimentally tested or theoretically investigated.

For the GE/*h*-BN multilayers, the GE and *h*-BN layers are stacked upon each other and interact through the weak van der Waals forces. By tuning the interlayer distance and the stacking pattern, the electronic properties of the GE/*h*-BN multilayers can be modified, which indicates large potential for building high-performance nanoelectronics [43]. In fact, recently, various van der Waal heterostructures (Fig. 2.4) similar to the GE/*h*-BN multilayers, have become of great interest and one frontier of the nanomaterial field [44].

Fig. 2.4. Atomistic schematic of van der Waal heterostructures obtained by stacking different types of 2D nanomaterials [44].

With the availability of various types of 2D nanomaterials, many van der Waal heterostructures besides the hybrid GE/*h*-BN multilayers have been designed, synthesized

and characterized. For example, the GE/MoS₂ hybrid multilayers have been recently fabricated for the application of electronic logics [45] and memory devices [46]. It is believed that with the increase in the understanding of the basic physics in pristine GE, more and more attentions will be driven to explore the properties and fabrications of GE-based nanocomposites as well as their potential applications.

2.2. Thermal transport at the nanoscale

Transport or conduction of thermal energy requires carrier particles or waves that transfer energy from one region of space to another. In metals, the thermal transport is mainly governed by the electrons except in alloys that have extremely low electrical conductivity. In most electrical insulators or semiconductors as GE, the main heat carriers are phonons, in other words, the quantized lattice vibrations of atoms.

2.2.1. Phonons

2.2.1.1. Concepts of phonons

A phonon is a quantum mechanical description of the elementary vibrational motion in which atoms or molecules of a crystal lattice uniformly oscillate at a single frequency. Specifically, the motion of one individual atom in the crystal lattice can be represented in the harmonic approximation as a superposition of the elementary vibrational motions each of which has a well-defined energy and crystal momentum. These elementary vibrations are known as normal modes in classical mechanics. When quantized, they are referred to as phonons or phonon modes, a term that is also often used informally to describe

classical lattice vibrations. Due to the wave-particle duality of quantum mechanics, phonons possess particle-like as well as wave-like properties.

Phonons carry energy as they propagate through the crystal and thus contribute to the thermal conductivity. According to the displacement directions of the normal vibration modes, phonons in 2D nanomaterials can be categorized into longitude (L) modes, transverse (T) modes and flexural out-of-plane (Z) modes. The L modes correspond to the atomic displacements along the phonon propagation direction, whereas the T modes correspond to the displacements perpendicular to the propagation direction. In bulk 3D solids, the T modes can have two equivalent polarizations. However, in 2D nanomaterials, the out-of-plane atomic displacements are allowed which then correspond to the Z modes. The modification of these modes (especially the Z modes) through chemical functionalization, strain engineering and defect engineering leads to many of the unique thermal properties of GE.

An important concept related to phonons is the density of states (DOS), also known as phonon spectrum. In solid-state and condensed matter physics, the DOS of a system describes the number of states per interval of energy that are available to be occupied. The energy E of phonons depends on their frequencies ω , and thus the DOS of the phonons are conventionally described in ω rather than E . A high DOS at a specific frequency level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that frequency level. Figure 2.5 shows the phonon DOS of GE. Most of the thermal properties of GE can be understood by analyzing its phonon behaviors.

Fig. 2.5. Phonon DOS of GE [47].

2.2.1.2. Phonon dynamics and scatterings

Under the harmonic approximation of lattice vibrations, phonons can be regarded as the quantum eigenstates of the atomic system. Hence, they can propagate freely without dissipation, leading to infinitely large thermal conductivity for a purely harmonic solid, which obviously disobeys the nature rules. For a solid to have finite thermal conductivity, as all the solids do, the dissipation of its photons must occur in the form of scattering either by themselves or its geometrical defects or constrains including point defects, dislocations, grain boundaries, surfaces and interfaces.

The existence of phonon scattering is also indicated by the Fourier's law of thermal conduction $J = -\lambda \nabla T$, where J is the heat flux, λ is the thermal conductivity and ∇T is the temperature gradient along the heat flux direction. The Fourier's law implies that the thermal energy does not proceed freely along a specimen, but diffuses as it propagates. Otherwise, the heat flux would only depend on the temperature difference ΔT at the two

ends of the specimen rather than the temperature gradient which includes the effects of sizes.

For the phonon-phonon scattering, there are two possible processes involved, namely, the normal scattering process and the Umklapp scattering process, both of which are schematically shown in Fig. 2.6. The grey square delineates the first Brillouin zone. Two incoming phonons with the wave-vectors $\vec{K}_1$ and $\vec{K}_2$ collide with each other and one outgoing phonon with a wave vector $\vec{K}_3$ is created. If the outgoing phonon wave vector $\vec{K}_3 = \vec{K}_1 + \vec{K}_2$ and stays inside the first Brillouin zone, the scattering process is called the normal scattering process.

Fig. 2.6. Schematics of (a) normal and (b) Umklapp phonon scattering processes.

On the other hand, for the Umklapp scattering process, the phonon momenta of the two incoming phonons are larger than those for a normal process, and the sum of their wave vectors $\vec{K}_1$ and $\vec{K}_2$, indicated as $\vec{K}_3'$ in Fig. 2.6 (b), will fall outside the first Brillouin zone. Physically, a wave vector outside the first Brillouin zone can be

equivalently transformed to a vector inside by the addition of a reciprocal lattice vector $\vec{G}$, i.e., $\vec{K}_3' = \vec{K}_3 + \vec{G}$. As a result, for the Umklapp scattering process, $\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G}$. In the normal scattering process, the phonon momentum is conserved, but in the Umklapp process, the total phonon momentum changes direction as if the outgoing phonon is reflected by the boundaries of the first Brillouin zone. Hence, it is the Umklapp process that mainly contributes to the resistance of thermal transport, especially for materials with no defects or low defect concentrations.

By treating phonons as pseudo-particles traveling through a solid, the basic kinetic theory can be applied to get an expression for the thermal conductivity λ , known as the Debye equation, $\lambda = C_v \nu \mathcal{A} / 3$. Here, C_v is the constant volume heat capacity; ν is the group velocity of the phonons which can be approximated by the velocity of sound for most solids; $\mathcal{A}$ is the length of mean free path (MFP) of the phonon which represents the characteristic length for the scatterings of phonons. The specific heat and the phonon group velocity can easily be determined, and are essentially independent of the structure of a system as it approaches the nanoscale. Reversely, the MFP length $\mathcal{A}$ of a material is very sensitive to its atomic structures, and is related to the phonon relaxation time τ and group velocity as $\mathcal{A} = \tau \nu$. In the approximation of τ , the effects of various scattering mechanisms which limit $\mathcal{A}$ are additive in terms of $\tau^{-1} = \sum \tau_i^{-1}$ according to the Matthiessen rule [48], where i numbers all the scattering processes including phonon-phonon scattering and phonon scattering by point defects, dislocations, grain boundaries and so on.

2.2.1.3. Phonon thermal conductivity

The thermal conductivity λ calculated from the Debye equation is a rather rough estimation since it uses simple average values of A and v for all the phonons. This rough estimation may be well applicable for bulk materials; however, it could lead to large errors when nanomaterials are investigated of which atomistic structures and dimensions play a significant role in determining A , v and C_v , and no average values could be used. In such circumstances, it is necessary to calculate the thermal conductivity by exploring the properties of individual phonons.

For example, the phonon heat flux in a GE nanosheet can be calculated according to the expression [49]

$$\vec{J} = \frac{1}{L_x L_y L_z} \sum_{s, \vec{q}} \vec{v}(s, \vec{q}) \hbar \omega_s(\vec{q}) n[\vec{q}, \omega_s(\vec{q})] \quad (2.1)$$

where $L_x L_y L_z$ is the volume of the GE nanosheet with L_x , L_y and L_z being the length, width and thickness, respectively; $\vec{v} \hbar \omega$ is the energy carried by one phonon with $\vec{v}$, $\hbar$ and ω denoting the phonon group velocity, Plank constant and frequency, respectively; $n[\vec{q}, \omega_s(\vec{q})]$ is the number of phonons in the $(s, \vec{q})$ mode with s denoting the polarization of the phonon dispersion branches and $\vec{q}$ the wave vector.

According to the Boltzmann equation and the time relaxation approximation, $n[\vec{q}, \omega_s(\vec{q})]$ can be obtained as

$$n = -\tau [\vec{v}(s, \vec{q}) \nabla T] \frac{\partial n_{BE}(T)}{\partial T} . \quad (2.2)$$

Here, $n_{BE}(T) = 1/\{\text{Exp}[\hbar\omega/(k_B T)] - 1\}$ is the Bose-Einstein distribution function at the temperature T , τ is the relaxation time, and ∇T is the temperature gradient along the heat flux direction.

The substitution of Eq. (2.2) into Eq.(2.1) leads to

$$\vec{J} = -\frac{1}{L_x L_y L_z} \sum_{\beta} (\nabla T)_{\beta} \sum_{s, \vec{q}} \tau v_{\beta}(s, \vec{q}) \frac{\partial n_{BE}(T)}{\partial T} \vec{v}(s, \vec{q}) \hbar \omega_s(\vec{q}). \quad (2.3)$$

By using the following macroscopic definition of the thermal conductivity

$$J_{\alpha} = -\lambda_{\alpha\beta} (\nabla T)_{\beta}, \quad (\alpha, \beta = x, y, z), \quad (2.4)$$

the thermal conductivity tensor can be obtained as

$$\lambda_{\alpha\beta} = -\frac{1}{L_x L_y L_z} \sum_{s, \vec{q}} \tau v_{\alpha}(s, \vec{q}) v_{\beta}(s, \vec{q}) \frac{\partial n_{BE}(T)}{\partial T} \hbar \omega_s(\vec{q}). \quad (2.5)$$

The diagonal element of the thermal conductivity tensor which corresponds to the phonon flux along the temperature gradient direction is given by

$$\lambda_{\alpha\alpha} = -\frac{1}{L_x L_y L_z} \sum_{s, \vec{q}} \tau v_{\alpha}^2(s, \vec{q}) \cos^2 \varphi \frac{\partial n_{BE}(T)}{\partial T} \hbar \omega_s(\vec{q}), \quad (2.6)$$

where φ is the angle between the temperature gradient and the direction of $v(s, \vec{q})$.

Usually, the thermal conductivity calculation based on Eq. (2.6) is called the complete phonon dispersion relation method as the dispersion relation $\omega_s(\vec{q})$ is explicitly included. In addition, the phonon group velocity $v(s, \vec{q})$ is also obtained by taking differentiation of $\omega_s(\vec{q})$ with respect to the wave vector $\vec{q}$, i.e., $v(s, \vec{q}) = \partial\omega(\vec{q})/\partial\vec{q}$. In the calculation of λ , the dispersion relation is usually expressed in different approximations such as the simple linear dispersion relation in the Debye model for density of phonon states. For more accurate dispersion relation expressions, experimental measurements are

normally needed for numerical fittings which can only be conveniently applied to monatomic materials with simple lattice structures.

2.2.2. Size effect

For bulk materials, their thermal conductivity is an intensive property and independent of the size and geometry, just as other physical properties such as electrical conductivity, density and specific heat capacity. However, as the material size L approaches the nanoscale, the thermal conductivity λ diverges with L . Such size effect is prominent when L is small, especially when it is much smaller than the MFP length Λ of the phonon. Under such circumstance, phonons propagate through the material in a ballistic manner and are seldom scattered by themselves given that no defects exist. Hence, the MFP length Λ is mainly limited by the size of the material and its λ increases dramatically with the size according to the kinetic theory of thermal conductivity, i.e., the Debye equation $\lambda = C_V v \Lambda / 3$.

A relationship of $\lambda \propto L^\beta$ has been found for both 1D nanotubes/nanowires [50, 51] and 2D nanosheets/nanoribbons [52], with the value of β depending on various parameters including the temperature, material size and geometry. It was reported that as the temperature increases from 300 to 800 K, β decreases from 0.40 to 0.26 for a (5,5) single-wall CNT. Similar phenomenon has also been observed in Si nanowires. At room temperature, their thermal conductivity increases almost linearly ($\beta = 1$) with their length when it is smaller than 60 nm. However, with the temperature increased to 1000 K,

β dramatically decreases to 0.15 [50]. For GE, the relationship of $\lambda \propto L^\beta$ was also identified and β was found to be in the range of 0.35-0.47 [52].

When the material size increases to be much larger than the MFP length λ , phonons undergo many scattering events as they propagate and the thermal transport transfers from ballistic to diffusive. Under this condition, the size dependence of the thermal conductivity reduces and even vanishes as the material approaches the macroscale.

2.2.3. Surface and interface effects

One of the key characteristics of nanomaterials is the high surface to volume ratio, which imposes significant confinement on the phonon transport due to the phonon scatterings at the boundaries. It has been demonstrated that due to such boundary scattering effect, the thermal conductivity λ of Si nanowires is about two orders of magnitude lower than that of bulk Si [53]. By increasing the surface area of Si nanowires through creating holes inside them [54] or roughening their surfaces [55], ultra-low thermal conductivity can be achieved, making them a good candidate in thermoelectric applications.

Similarly, owing to the strong phonon scattering at the edges, the λ of GE nanoribbons was found to be lower than that of GE nanosheets [56]. In addition, the λ of zigzag GE nanoribbons is also larger than that of armchair nanoribbons because of their higher phonon scattering rates at the edges [52, 57]. However, such anisotropy phenomenon disappears and the phonon-edge scattering becomes negligible as compared to the internal phonon-phonon scattering when the widths of the nanoribbons become larger than 100 nm [56]. Furthermore, both MD simulation and theoretical calculation

have indicated that the thermal conductivity of GE can be significantly suppressed by roughening its edges [56]. Through the passivation of the edges of GE nanoribbons with hydrogen atoms, their thermal conductivity can further be reduced [58].

In addition to the surfaces or edges, interfaces inside nanomaterials also play a critical role in their thermal transport, especially for composite nanomaterials where sharp interfaces are usually formed with large atomic mass or structure mismatches. As the phonons encounter an interface, they transmit through or are reflected back. In either case, phonon scatterings will occur and thermal resistance will often be generated.

At the macroscale, phonon transmission at the interface can be understood by two theoretical models: the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM). The AMM assumes that the transmission of phonons across the interface only depends on the acoustic impedance mismatch on both sides of the interface; while the DMM considers that the phonons are diffusively scattered by the interface and their transmission coefficient is only determined by the mismatch of the phonon DOS across the interface. Both models can be applied to predict the phonon transmission coefficient and thus the interface thermal transport behavior. However, the predictions are purely based on the bulk properties of the materials forming the interface with the effect of detailed interface structure being ignored.

In practice, interfaces including grain boundaries and those between dissimilar materials are neither flat nor crystallographically coherent. At the nanoscale, the atomic structures of interfaces, such as bonding type, coupling strength, roughness and curvature, can significantly affect their thermal transport capability. The previous study has demonstrated that thermal transport between graphene and polymer can be largely

enhanced by forming covalent bonds between them [59]. The interfacial thermal conductance between CNTs and bulk Si was found to be much larger when small pressure was applied to increase the interface coupling [60]. By modifying the interface roughness of the superlattice-structured Si/Ge nanowire, an efficient control of its thermal conductivity was obtained [61].

2.2.4. Atomistic structural effect

In practical applications of nanomaterials, their atomic structures may suffer from certain levels of distortion caused by strain engineering, chemical functionalization, doping and inevitable microstructural defects. Such structure distortions can significantly affect the phonon transport behaviors by either changing the interaction between the phonons or creating additional phonon scattering centers.

Strain engineering may be one of the most meaningful approaches to pursue because of its continuous tunability and its flexibility to realize. The idea of applying strain to tune material properties has been explored for a long time. For example, strained Si has been long used to enhance the electron mobility of the Si-based field-effect transistor [62]. Recent MD simulation has identified that the thermal conductivity of GE nanoribbons decreases dramatically under tensile strain due to the softening effect of both longitudinal and flexural phonon modes [63]. When the phonon modes are softened, more phonons are squeezed into a narrower frequency range, leading to enhanced scattering between the phonons. This softening effect has later been utilized to construct thermal rectifiers by asymmetrically applying tensile strain along GE nanoribbons [64].

Interestingly, in contrast to the counterpart of GE, SE exhibits a reverse thermal response under tensile strain, i.e., its thermal conductivity first increases rather than decreases and then stabilizes. This anomalous thermal response was attributed to the stiffening effect of the flexural phonon modes of SE, which counteracts the softening effect of the longitudinal modes and facilitates the thermal transport [65]. In addition to phonon softening and stiffening, strain also changes the morphology of nanomaterials especially thin films, and thus tunes their thermal properties. For example, when GE nanoribbons or CNTs are subjected to compressive strain, surface waviness[63] or buckling [66] can be induced to serve as phonon scattering sources and reduce the thermal conductivity.

Besides strain engineering, the approaches including chemical functionalization, doping and defective engineering have also been of great interest. For instance, as one of the widely applied chemical functionalization methods, hydrogenation has been found to be efficient in tuning the thermal properties of GE. By conducting MD simulations, Pei *et al.* [67] have found that the thermal conductivity of GE greatly depends on the hydrogen distribution and coverage. For the random distribution, it has been demonstrated that the hydrogenation coverage of 20% for GE can cause almost 70% reduction in its thermal conductivity [68]. Such reduction can be even larger when the hydrogenation is arranged in ordered patterns [67, 69]. The dramatic reduction caused by the random hydrogenation of GE has been attributed to the introduction of sp^3 bonds into its sp^2 network which serve as randomly distributed phonon scattering centers [68]. For the patterned hydrogenation, the large thermal resistance caused by the severe phonon scattering at the interfaces between the hydrogenated and pristine GE domains has been found to be the main reason

for the reduction of the thermal conductivity of hydrogenated GE [67]. In addition, such phonon scattering is asymmetric about the interface and can lead to its thermal rectification effect [70]. When hydrogenation is only applied at the edges of GE, its thermal conductivity can also be significantly affected due to modified phonon scatterings at the boundaries [56].

With the fast development of the experimental techniques, the distribution of the functional groups, doping atoms and defects can be well controlled even at the nanoscale, which greatly facilitates the manipulation and engineering of the phonons. As a result, the phonon behaviors can be controlled or designed, which may lead to novel thermal management applications such as high-performance thermal rectifiers and thermoelectric devices.

2.3. Atomistic simulations of thermal transport

Atomistic simulations are capable of predicting the thermal transport properties of materials through a comprehensive understanding of its atomic structure and interatomic interactions. So far, various atomistic simulation approaches have been developed for the study of the thermal transport properties of nanomaterials.

2.3.1. Simulation approaches overview

Various simulation approaches for the investigation of material thermal properties are characterized in Fig. 2.7 [71]. The first class includes the Boltzmann transport equation approach and the non-equilibrium Green's function approach. These two approaches predict the thermal properties starting from the understanding of the fundamental of

phonon properties by solving the lattice dynamics equations. The second class calculates the thermal properties directly through MD simulation, such as the equilibrium Green-Kubo approach and the non-equilibrium MD approach (known as the direct approach).

Fig. 2.7. Classifications of the atomistic simulation approaches for calculating thermal properties of materials [71].

In the approaches of the first class, the physics of phonon transport and scattering are incorporated during the calculation in an explicit manner such as the Monte Carlo (MC) method, and thus *a priori* understanding of the phonon transport process is required. For a material with simple lattice structures, such requirement is easy to meet. However, when there are structure disruptions such as sharp interfaces, a reliable description of the phonon transport behavior is usually difficult to obtain.

In contrast, the MD simulation of the second class merely involves the integration of the Newton's equations of motion with respect to time for a group of atoms interacting with each other through an empirical potential function. In addition, MD simulation can usually handle both small and large systems, while the system size that can be modeled by

the approaches of the first class is severely limited because their computational load increases in a manner of $\sim k^2 \times N^4$, where k is the number of points in the Brillouin zone and N is the number of atoms [72].

For better comparison of these two classes of simulation approaches, three typical simulation methods that have been recently widely adopted to predict the thermal conductivity of nanostructured materials are briefly discussed below, including the MC simulation approach, equilibrium Green-Kubo approach and the direct non-equilibrium MD simulation approach. Based on the discussion, the suitable method is chosen for this PhD study.

2.3.2. Mento Carlo simulation approach

The theoretical analysis of phonon transport often starts with the Boltzmann transport equation [73]. However, a closed-form solution of this equation usually requires several critical assumptions and simplifications which may lead to significant deviations of the results from experimental observations, especially for materials with relatively complex geometry and lattice structure, and those containing multiple types of defects.

The MC method was initially used to numerically solve the Boltzmann transport equation for electron transport [73]. Since then, this method has found wide applications in handling transport problems of particles. For thermal transport properties, the MC method has been successfully applied to bulk materials [74], thin films [75, 76], nanowires [73, 77] and nano-composites[78].

When the MC method is used to solve the transport problem of phonons, they are treated as randomly distributed particles drifting in the real space. The flowchart of the

MC simulation of phonon transport is presented in Fig. 2.8. At the beginning, a simulation domain is specified according to the simulation system and the desired simulation parameters such as system sizes, boundary conditions and temperature. The simulation domain is then uniformly discretized into many cells along the phonon transport direction.

Fig. 2.8. Flowchart of the MC simulation of phonon transport [79].

In each cell, phonons are initialized according to the desired temperature T_i of the cell. The expected number of phonons in the i -th cell in the simulation domain is calculated as [79]

$$N_i = V \sum_s \int P_s(\omega) n_{BE}(T_i) d\omega . \quad (2.7)$$

Here, V is the volume of the cell, $n_{BE}(T_i)$ is the Bose-Einstein distribution function at the temperature T_i as stated before, and $P_s(\omega)$ is the phonon density state along the phonon branch S . Accordingly, the total phonon energy in this cell can be written as

$$E_i = V \sum_s \int P_s(\omega) n_{BE}(T_i) \hbar \omega d\omega . \quad (2.8)$$

To fully describe these phonons, their group velocity, position, frequency, polarization and wave vector have to be assigned. The group velocity can be obtained by taking differentiation of the dispersion relation, but the other quantities are generated randomly by following certain rules. For example, the position $\vec{r}$ of a phonon resides in the i -th cell is given by [80]

$$\vec{r} = \vec{r}_i + R_1 \vec{a} + R_2 \vec{b} + R_3 \vec{c} , \quad (2.9)$$

where $\vec{r}_i$ is the position vector of the reference vertex of the i -th cell; $\vec{a}$, $\vec{b}$ and $\vec{c}$ are the edge-vectors from the reference vertex to its neighboring vertices, while R_1 , R_2 and R_3 are random numbers in the range of 0 to 1.

After the initialization, phonons are allowed to drift for a small time step Δt . This time step is so small that a phonon is unlikely to scatter more than once within it. Hence, phonon drift and scattering are separated, and all the phonon scattering events can be treated cumulatively for the entire simulation domain after the current simulation time step.

The phonon drift is easy to implement in the MC simulation since only the group velocity and drift direction are required. However, the phonon scattering is much more difficult to realize. In the MC simulation, the phonon scattering is treated at the end of each time step by calculating the scattering probability $g_{scat}(\omega)$ based on [79]

$$g_{scat}(\omega) = 1 - \exp[-\tau^{-1}(\omega)\Delta t] \quad , \quad (2.10)$$

where τ is the phonon relaxation time as discussed in Section 2.1.1. To determine whether a phonon is scattered during the drift process, a random number is drawn and compared with $g_{scat}(\omega)$. Meanwhile, another random number is generated to determine the scattering mechanism (boundary scattering, defect scattering or phonon-phonon scattering).

For the phonons that experience the scattering event, they are either replaced or have their frequency and wave vector changed, i.e., re-initialized, to conserve the energy in each cell. The drift, scattering and re-initialization process is repeated for enough time until a steady state of the whole simulation system is achieved. The steady state can be either equilibrium or non-equilibrium, depending on the desired temperature of each discretized cell. For a steady state with a linear temperature gradient along the transport direction of the phonons, the thermal conductivity can be calculated by injecting them at the hot end of the simulation domain and observing their transport behaviors [80].

As one typical method of predicting the thermal properties by understanding the lattice dynamics, i.e., the phonons, the MC simulation suffers from the disadvantages that a numerical expression of the phonon dispersion is always required in order to obtain reasonable phonon numbers and distributions in both the spatial and spectral spaces. In

addition, to address the scattering events, an explicit expression of the scattering rate $\tau^{-1}(\omega)$ affected by different scattering mechanisms should also be provided. Generally, these two requirements are difficult to meet for GE-based nanomaterials, especially with many factors being considered, including strain, chemical functionalization, interface and defects.

2.3.3. Equilibrium Green-Kubo approach

The net flow of heat in a solid, given by the heat flux J , fluctuates around zero at the equilibrium state. The damping speed of the fluctuations physically reflects the thermal resistance of a material. In the equilibrium Green-Kubo approach, the thermal conductivity is calculated by tracking the dissipation time of these fluctuations. For an isotropic material, its thermal conductivity obtained by the Green-Kubo approach is given by [81]

$$\lambda = \frac{1}{3k_B VT^2} \int_0^\infty \langle \vec{J}(0) \vec{J}(t) \rangle dt, \quad (2.11)$$

where $\langle \vec{J}(0) \vec{J}(t) \rangle$ is known as the heat flux autocorrelation function and the angular brackets denote an ensemble average over time. Here, k_B is the Boltzmann constant, V is the system volume and T is the temperature. In materials where the fluctuations are long lived, in other words, the phonon relaxation time $\tau(\omega)$ is large, and the autocorrelation function $\langle \vec{J}(0) \vec{J}(t) \rangle$ decays slow. Accordingly, the thermal conductivity is large. In contrast, the fluctuations in materials such as amorphous solids are quickly damped,

indicating a small phonon relaxation time $\tau(\omega)$. Hence, a low thermal conductivity is usually present.

In Eq. (2.11), the heat flux $\vec{J}$ can be calculated by [82]

$$\vec{J} = \frac{1}{V} \frac{d}{dt} \sum_i \vec{r}_i E_i, \quad (2.12)$$

where the summation is over all the particles in the simulation system, and $\vec{r}_i$ and E_i are the position vector and the energy of the i -th particle, respectively. For a pair potential, the above equation can be rewritten as [82]

$$\vec{J} = \frac{1}{V} \left[\sum_i e_i \vec{v}_i + \frac{1}{2} \sum_{i < j} (\vec{F}_{ij} \cdot (\vec{v}_i + \vec{v}_j)) \vec{r}_{ij} \right], \quad (2.13)$$

where $\vec{v}_i$ is the velocity vector; $\vec{F}_{ij}$ and $\vec{r}_{ij}$ are the inter-particle force and separation vectors, respectively. This form of heat flux can be readily implemented in an MD simulation.

One advantage of this approach is that it requires much smaller simulation cell sizes than the non-equilibrium MD approach, and thus is desirable for perfect crystals like Si and diamond with long phonon MFP. However, this approach suffers from poor convergence and the difficulty in defining the heat flux when complicated potential functions are used. Moreover, for an inhomogeneous system containing, for example, an interface, this approach treats the system as a homogeneous system and computes an average thermal conductivity over the entire system. Hence, it fails to investigate the detailed phonon transport behaviors at the interface. In consideration of these facts, it appears that this approach is not suitable to study the thermal properties of 2D nanomaterials with the presence of impurities and interfaces considered.

2.3.4. Direct MD simulation approach

The non-equilibrium MD approach and the equilibrium Green-Kubo approach are mostly frequently used during MD simulation to directly calculate the thermal conductivity of a material. The non-equilibrium MD approach is similar to the experimental method of measuring the thermal conductivity. In this approach, one region of the simulation cell is heated up while another region with some distance away is cooled down. When the system reaches a stable state, a temperature profile between the hot and cold regions can be established, from which the temperature gradient can be determined. If the heat flux J needed to maintain the temperature gradient is known, the thermal conductivity can be calculated based on the Fourier's law.

This approach is direct and can be easily implemented in MD simulation since only classical quantities such as force, velocity and position are calculated to obtain the temperature and heat flux. In addition, no significant assumption is made during the calculation of the thermal properties. Implementation details of this approach will be given in the following chapters when is applied and thus are not presented here.

2.3.4.1. Fundamentals of MD simulation

MD simulation is a technique used to investigate the structure, dynamics, and transport properties of many-body systems, by calculating the motion of the atoms in a molecular assembly. Such calculation is realized based on the numerical integration of Newton's equation of motion:

$$m \frac{d^2 \vec{r}_i}{dt^2} = - \frac{\partial V}{\partial \vec{r}_i} . \quad (2.8)$$

Here, $m, \vec{r}_i$ and V are the mass of the i th atom, its position vector and the interatomic potential. The integration scheme used for Eq. (2.8) is the Verlet algorithm which predicts the position at $t + \delta t$ if given the position at the earlier time t and $t - \delta t$. In this algorithm, the Taylor expansion series of $\vec{r}_i$ at both $t + \delta t$ and $t - \delta t$ till the third order are utilized as

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t)\delta t + \frac{\vec{a}_i(t)}{2}\delta t^2 + \frac{\vec{b}_i(t)}{6}\delta t^3 + O(\delta t^4), \quad (2.9)$$

$$\vec{r}_i(t - \delta t) = \vec{r}_i(t) - \vec{v}_i(t)\delta t + \frac{\vec{a}_i(t)}{2}\delta t^2 - \frac{\vec{b}_i(t)}{6}\delta t^3 + O(\delta t^4). \quad (2.10)$$

The summation of Eqs. 2.3 and 2.4 produces the expression of the position $\vec{r}_i(t + \delta t)$ in terms of $\vec{r}_i(t)$ and $\vec{r}_i(t - \delta t)$ as

$$\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \vec{a}_i(t)\delta t^2 + O(\delta t^4). \quad (2.11)$$

Similarly, by utilizing the Taylor expansion series of $\vec{r}_i$ at both $t + \delta t$ and $t - \delta t$ to the first order, the velocity $\vec{v}_i$ can be obtained as

$$\vec{v}_i(t) = \frac{\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)}{2\delta t} + O(\delta t^2). \quad (2.12)$$

Compared with other integration algorithm, the Verlet algorithm is simple, easy to implement, stable and time reversible, and thus has been widely applied.

One problem of the Verlet algorithm is that the estimation error of the position is on the order of $O(\delta t^4)$, but that of the velocity is on the order of $O(\delta t^2)$. To solve this problem, several improved Verlet algorithms have been developed. One of such algorithms is the Velocity Verlet algorithm which can be expressed as

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i\delta t + \frac{\vec{a}_i}{2}\delta t^2, \quad (2.13)$$

$$\vec{v}_i(t + \delta t / 2) = \vec{v}_i(t) + \frac{\vec{a}_i}{2} \delta t, \quad (2.14)$$

$$\vec{a}_i(t + \delta t) = \left(-\frac{1}{m}\right) \frac{\partial V}{\partial r_i(t + \delta t)}, \quad (2.15)$$

$$\vec{v}_i(t + \delta t) = \vec{v}_i(t + \delta t / 2) + \frac{\vec{a}_i}{2} \delta(t + \delta t) \delta t. \quad (2.16)$$

The Velocity-Verlet algorithm is simpler, faster and requires less computer storage space and has been more and more adopted. This algorithm is adopted throughout this PhD study.

According to the principles of MD simulation, its general workflow can be divided into the following steps:

- (1) Initiating the positions and velocities of the atoms, i.e., setting $\vec{r}_i(0)$ and $v_i(0)$;
- (2) Choosing a proper potential energy function and calculating the interatomic forces;
- (3) Solving the Newton's equations of motion to update the positions and velocities of the atoms, i.e., obtaining $\vec{r}_i(dt)$ and $v_i(dt)$;
- (4) Recording instantaneous quantities of concern and repeating steps 2 to 4 till the end of the simulation;
- (5) Processing the recorded instantaneous quantities to investigate the behaviors and properties of the entire system.

In this study, the simulation will be conducted by using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package. It is a free and open-source classical MD code that models an ensemble of particles in a liquid, solid, or gaseous state. It can model atomic, polymeric, biological, metallic, granular, and coarse-grained systems using a variety of force fields and boundary conditions. It allows

modification of its source codes according to specific simulation requirements. Meanwhile, it is designed to run on multiple processors to accelerate the simulation. This package is more and more widely used due to its high efficiency and flexibility, and thus is adopted in this study. High-performance computing clusters will be used to improve computational efficiency for systems of large size.

2.3.4.2. Potential functions

The advantages of MD simulation lie in its high speed and simplicity, as well as in its flexibility and versatility in the choice of the atomic potential energy functions (or potentials for short). Generally, the total potential energy of a system can be decomposed as

$$E = \sum_i V_1(\vec{r}_i) + \sum_{i<j} V_2(\vec{r}_i, \vec{r}_j) + \sum_{i<j<k} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots \quad , \quad (2.17)$$

where the first term represents the one-body contribution to the total potential energy and is usually related to an external field such as an electric or magnetic field. The second and third terms represent the two-body and three-body atomic interactions, respectively. The choice of the potential function usually depends on the problem, for example, the type of the atomic structure and the atomic element. Next, the potential functions that will be used in this PhD research are presented and briefly discussed. All these potentials have been

(a) Lennard-Jones potential

The Lennard-Jones (LJ) potential [83] is one of the simplest potential functions used in condensed-matter physics. Its total energy contains only the two-body interaction term:

$$E = \sum_{i<j} V_2(\vec{r}_i, \vec{r}_j), \quad (2.18)$$

with

$$V_2(\vec{r}_i, \vec{r}_j) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]. \quad (2.19)$$

Here, ε is the energy that reflects interaction strength of an atom pair; σ is the equilibrium interatomic distance; r_{ij} denotes the distance between the i th and j th atom.

Although simple, the LJ potential is usually adopted to model non-covalent interactions between the atoms or molecules. In principle, all the atoms inside the simulation region can interact. However, for a system containing N atoms, $N^2 / 2$ interatomic forces have to be calculated in each time step, which is usually computationally costly. Thus, the LJ potential is usually truncated at a cut-off radius which usually ranges from 2.5σ to 5.5σ .

(b) Stillinger-Weber potential

The Stillinger-Weber (SW) potential [84] is one of the first potentials that attempt to model a semiconductor with a classical model. The SW potential contains both two-body and three-body interactions and can be expressed as

$$E = \sum_{i < j} V_2(\vec{r}_i, \vec{r}_j) + \sum_{i < j < k} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k), \quad (2.20)$$

with

$$V_2(\vec{r}_i, \vec{r}_j) = A_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^p - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^q \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - \sigma_{ij} a_{ij}} \right), \quad (2.21a)$$

$$V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \lambda_{ijk} \left(\cos \theta_{ijk} + \frac{1}{3} \right)^2 \exp \left(\frac{\gamma_{ij}}{r_{ij} - \sigma_{ij} a_{ij}} \right) \exp \left(\frac{\gamma_{ik}}{r_{ik} - \sigma_{ik} a_{ik}} \right). \quad (2.21b)$$

In the two-body term, the parameters σ_{ij} is the equilibrium interatomic distance, while $a_{ij}\sigma_{ij}$ denotes the cutoff distance. In the three-body term, θ_{ijk} is the angle centered on the i th atom. The remaining parameters A, B, p, q, λ and γ are varied to modify the two-body and three-body interactions according to the interatomic distances and angles.

The SW potential was initially developed for the study of Si crystals. Since then, it has been widely used due to its simplicity and fairly realistic description of the atomic interaction of Si atoms. However, for the initial SW potential, its three-body term defines only the equilibrium configurations based on the diamond-like tetrahedral lattice structure and thus it is difficult to be applied to other lattice structures. Nevertheless, the concepts brought by the SW potential that uses only geometrical quantities such as distances and bond angles as variables to establish potential functions have gained big popularity. Based on these concepts, new SW potentials have been developed [85, 86], with either new energy terms or new parameterizations, to be applicable for a wider range of materials.

(c) Tersoff potential

The Tersoff potential [87] was developed with the focus on the covalent bonds in semiconductor systems. It is based on the concept of bond order which describes that the bond strength between two atoms is not a constant but depends on the local environment. In other words, the Tersoff potential considers the effect of all the nearest neighbors of an atom when calculating its interaction with other atoms, although it only contains a two-body term.

The analytical form of the two-body term of the Tersoff potential is shown as follows

$$V_2(\vec{r}_i, \vec{r}_j) = f_c(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \quad (2.22a)$$

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} < R - D \\ \frac{1}{2} \left\{ 1 - \sin \left[\frac{\pi}{2} \frac{(r_{ij} - R)}{D} \right] \right\}, & R - D < r_{ij} < R + D, \\ 0, & r_{ij} > R + D \end{cases} \quad (2.22b)$$

$$f_R(r_{ij}) = A \exp(-\lambda_1 r_{ij}), \quad (2.22c)$$

$$f_A(r_{ij}) = B \exp(-\lambda_2 r_{ij}), \quad (2.22d)$$

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}}, \quad (2.22e)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_c(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3], \quad (2.22f)$$

$$g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (\cos \theta_{ijk} - \cos \theta_0)^2]}. \quad (2.22g)$$

Here, $f_c(r_{ij})$ is the cutoff function which ensures only nearest-neighbor interactions with R and D being the cutoff distance parameters. The $f_R(r_{ij})$ and $f_A(r_{ij})$ functions represent the repulsive and attractive atomic interactions, respectively. The parameters A and B denote the cohesive energies, while λ_1 and λ_2 are lattice parameters.

The parameter b_{ij} represents the bond orders and is determined by the local coordination of atoms around the i th atom in the center. The idea of introducing the parameter b_{ij} is that in real systems, the strength of each bond depends on the local environment, i.e., an atom with more neighbors forms weaker bonds than an atom with fewer neighbors. In the expression of b_{ij} , ζ_{ij} is the effective coordination number of the

atoms, i.e., the number of the nearest neighbors, and takes into account the relative distance $r_{ij} - r_{ik}$ of two neighbors of the i th atom and the bond angle θ_{ijk} ; β and n are adjusting parameters chosen to reflect the realistic lattice structure and physical properties of a specific material; λ_3 is a cutoff parameter that determines the range for the calculation of ζ_{ij} . In the bond angle distribution function $g(\theta_{ijk})$, θ_0 is the equilibrium bond angle, and c and d are dimensionless parameters that determine the strength of the bond angle effect.

The Tersoff potential was calibrated firstly for Si systems and later for C systems, and was tested by calculating their cohesive energy, elastic constants, phonon frequencies, defect energies and migration barriers. The results obtained with this potential were in good agreement with experiments and *ab initio* calculations. So far, the Tersoff potential has been developed to be applied to various different systems, including Si-C hybrids, Si-O oxides, and several other semiconductor systems such as Ge and Ga.

(d) REBO potential

The reactive empirical bond-order (REBO) potential is an empirical potential that was initially developed for hydrocarbons and can model interatomic interactions in a variety of small hydrocarbon molecules as well as graphite and diamond lattice. This potential is a highly parameterized expression of the Tersoff potential with additional terms that correct for an inherent overbinding of radicals and include nonlocal effects. Following the expression of the Tersoff potential, the analytical form of the REBO potential is shown as

$$V_2(\vec{r}_i, \vec{r}_j) = V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij}) \quad (2.23a)$$

where the repulsive and attractive pair terms are given by

$$V_R(r_{ij}) = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}) \quad (2.23b)$$

and

$$V_A(r_{ij}) = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}). \quad (2.23c)$$

The term $\bar{B}_{ij}$ represents a many-body coupling between the bond from atom i to atom j and the local environment of atom i , and $R^{(e)}$ is the equilibrium distance between atoms i and j . The smooth continuous cut-off function $f_c(r_{ij})$ is used to restrict the pair potential to nearest neighbors and given by

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} < R^{(1)} \\ \frac{1}{2} \left\{ 1 + \cos \left[\frac{\pi(r_{ij} - R^{(1)})}{R^{(2)} - R^{(1)}} \right] \right\}, & R^{(1)} < r_{ij} < R^{(2)} \\ 0, & r_{ij} > R^{(2)} \end{cases} \quad (2.23d)$$

When S equals 2, the pair terms $V_R(r_{ij})$ and $V_A(r_{ij})$ reduce to the usual Morse potential which explicitly includes the effects of bond breaking, and also accounts for the anharmonicity of real bonds and the non-zero transition probability for overtone and combination bands. The term $D^{(e)}$ and β are parameters of the Morse potential.

(e) AIREBO potential

The AIREBO (short for adaptive interatomic reactive empirical bond order) potential has been widely used to describe the interactions in hydrocarbon systems including C nanostructures such as GE and CNTs [88]. This potential is an optimized version of the initial REBO potential which is developed based on the Tersoff potential.

The AIREBO potential is capable of describing both the weak van der Waals interactions between the non-bonded atoms, as well as the strong interactions between the atoms connected by covalent bonds. In addition, this potential considers the effect of the torsion caused by bond rotations, and thus is self-adaptive to the changes in bond angles during the lattice structure transformation. Therefore, the AIREBO potential is explicitly a four-body potential and can provide a more realistic description of the covalent bonding in hydrocarbon systems.

The AIREBO potential can be expressed as

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V_{ij}^{\text{REBO}} + V_{ij}^{\text{LJ}} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} V_{ijkl}^{\text{Torsion}} \right]. \quad (2.24)$$

The first term V_{ij}^{REBO} is the basic term of the entire potential and has an expression similar to the REBO potential. It describes the short-range interactions between two covalent-bonded atoms. The second term V_{ij}^{LJ} describes the long-range interactions between the non-bonded atoms and has the same expression as the LJ potential. The third term $V_{ijkl}^{\text{Torsion}}$ describes the interaction of the bond rotations caused by the changes of the bond angles.

2.4. Summary

General rules that govern the thermal transport at the nanoscale are reviewed. The concept of phonons is introduced with their dynamic and scattering behaviors briefly discussed. The effects of size, surface and interfaces, and atomistic structural effect on the

thermal properties of nanoscale materials including the GE and SE, are reviewed. The commonly used simulation approaches for the thermal transport at nanoscale are outlined and compared. The direct MD simulation approach is adopted and the fundamentals of MD simulation are presented.

Chapter 3. Thermal Conductivity of Hybrid Hydrogenated GE Nanosheets

Hydrogenation is one of the chemical functionalization methods and has been used to modify the mechanical and physical properties of GE. In this chapter, the in-plane thermal conductivity of hybrid hydrogenated GE sheets which consist of hydrogenated and unhydrogenated GE strips is studied. The effects of hydrogenation style and hydrogen coverage are investigated and understood by the phonon spectra analysis.

3.1. GE hydrogenation

Chemical functionalization by introducing external atoms or atomic groups has attracted attentions for controllably modifying the chemical, physical and mechanical properties of GE. Through chemical functionalization, the band gap of GE can be modified, transforming this highly conductive zero-gap material into a semiconductor [9, 89-92]. In addition, the attachable functional groups might also provide GE with other tailor-made mechanical and physical properties. For example, a single-side chemical functionalization on GE induces magnetic moments and results in the change of the magnetic property from antiferromagnetic to ferromagnetic [93].

Among all the functional groups including H, OH, CN, NH₂, CH₃ and COOH [91], atomic hydrogen has become the focus of recent studies, not only because of its efficiency in tuning the band gap of GE, but also for the potential of using GE as good hydrogen storage material [94, 95]. Recent progress in GE hydrogenation has indicated that it is

controllable and reversible [9, 96]. Moreover, patterned superlattice structure within a single sheet of partially hydrogenated graphene has also been successfully fabricated [97].

There are two typical styles of hydrogenation on GE reported till now. One style is to obtain graphane (GA), a fully double-side hydrogenated GE sheet with H atoms bonded to C atoms on both sides alternatively (Figs. 3.1(a) and (b)), where all the sp^2 bonds are transformed into sp^3 ones [9, 89]. The other style realizes graphone (GO), a single-side hydrogenated GE sheet (Fig. 3.1(c)), by utilizing the reversibility of the hydrogenation process, i.e., removing all the hydrogen atoms at one side of GA, in which half of sp^3 bonds are transformed back into sp^2 bonds [93]. Since the adsorption of hydrogen on GE sheets is reversible and can be applied controllably in different patterns, it is possible to construct “hybrid” GE sheets (HGSs) that contain fully- and/or semi-hydrogenated GE strips.

Fig. 3.1. Schematic of various sheets: (a) GE, (b) GA, (c) GO and (d) RGO.

As a result, a pristine GE sheet can be divided into several sub-domains or sub-strips with different thermal [67], electrical and magnetic properties [98]. This means that the insulating/antiferromagnetic and conducting/ferromagnetic properties can be integrated into a single GE sheet without the physical cutting and joining process. Thus, GE sheets

can be tuned via different hydrogenation styles and hydrogen coverages to design or develop a wide range of nanoelectronic devices.

With increased interest in using HGSs in nanodevices, a fundamental understanding of the thermal conductivity behavior of HGSs is critical, since the continuous development in nanodevices miniaturization calls for better heat dissipation and thermal management. It was found that hydrogenation reduces the thermal conductivity λ of GE significantly even at a relatively low hydrogen coverage [68]. In addition, the λ of HGSs depends on the hydrogenation pattern in terms of hydrogen coverage and the type and number of interfaces between strips [67, 70]. However, the effect of hydrogenation on λ has not been fully understood. In particular, no study has been conducted on λ of semi-hydrogenated GE sheets or HGSs that contain semi-hydrogenated GE strips. On the other hand, external elastic strain applied to GE-based materials has been found to alter their thermal properties by changing their morphologies [66, 99]. Meanwhile, interfacial strain due to partial hydrogenation can affect the morphologies of HGSs [100]. It is predicted such interfacial strain would also have an effect on their thermal properties. Therefore, the study presented in this chapter aims to understand the effect of the hydrogenation style and hydrogen coverage on the morphology and λ of HGSs via MD simulation.

3.2. Simulation model

In this work, both the GA and GO hydrogenation styles, which have been realized experimentally, are adopted to construct HGSs. In addition to the GA and GO styles, another hydrogenation style is proposed in which the sp^3 bonds in the GO sheet are rearranged to be on both sides (Fig. 3.1(d)). Since the hydrogenation of GE is revisable

[101] and controllable [102], this proposed style is also possible to be realized experimentally. In the rearranged GO sheet, named RGO sheet thereafter, the hydrogen atoms within one zigzag chain are located on the same side of the sheet while those within the neighboring chains are on the other side.

The HGS that contains both GE and GA strips is called GA-HGS, and so are GO-HGS and RGO-HGS. Figure 3.2 illustrates the model configuration of an HGS with the length $L_0 = 20\text{nm}$ and width $W_0 = 5\text{nm}$. A GA/GO/RGO strip is embedded in between two GE strips of which the length is along the heat flux direction. The width of the GA/GO/RGO strip is denoted by W , and the area fraction of the strip to the whole sheet is given by their width ratio $f = W/W_0$. Thus, the hydrogen coverage of the HGSs can be expressed by f .

Fig. 3.2. Schematic of an HGS. The GA/GO/RGO strip (red color) is embedded in between GE strips (grey color).

As mentioned in Section 2.2, the open-source LAMMPS package is used for conducting the MD simulation studies here and those in the following chapters. The AIREBO potential, which is embedded in the LAMMPS package, is applied to study the

thermal properties of HGSs [103]. The detailed expression of the AIREBO potential refers to Section 2.2.2.2. The initial configuration is constructed based on structural optimization of an HGS sheet, which will be explained in detail later. The periodic boundary condition is applied along both the width and length directions to mimic infinitely large GE nanosheets. Previous studies have shown that the thermal conductivity of GE nanosheets can also be affected by their width due to phonon scattering the edges [104, 105]. However, by applying the periodic boundary conditions, the width effect can be well eliminated because the vanishing of edges and thus the boundary scatterings.

At first, the initial configuration is equilibrated using the constant volume and temperature (NVT) ensemble at 300K for 50 ps with the time step $\Delta t = 0.5\text{fs}$. Upon realization of the equilibrium state, Afterwards, the system is switched to the constant volume and energy (NVE) ensemble to keep the energy conserved. A constant heat flux J is then imposed into the system at each time step by adding a small amount of heat $\Delta\xi$ into the heat source (with a thickness of 2δ) in the middle and meanwhile reducing $\Delta\xi/2$ from heat sinks (with a thickness of δ) at both ends. After enough simulation time, a stable temperature gradient ∇T is established along the heat flux direction. As a result, the thermal conductivity λ can be obtained based on Fourier's law $J = -\lambda\nabla T$ in which J is given by $J = \Delta\xi/(2A\Delta t)$ with A denoting the cross-section area, i.e., $\lambda = -\Delta\xi/(2A\Delta t\nabla T)$. In the area calculation, the HGSs are set to have the same thickness of 0.34 nm, which is the interlayer distance of graphite. This simulation approach falls in the non-equilibrium methods as illustrated in Fig. 2.7. During the modeling, structural optimization is used to get a suitable configuration for thermal

conductivity calculation, and realized based on the investigation of the morphologies of HGSs. Their primal configurations are constructed using the lattice parameter of GE and then relaxed at 300K.

3.3. Morphology

The simulation results show that all the HGSs deviate from the primal planar morphology and exhibit prominent flexures (Fig. 3.3). It is found that large periodic ripples are formed in all the HGSs upon relaxation. For the same width ratio, GA- and RGO-HGSs exhibit small wavelength periodic ripples due to the hydrogen distribution on both sides of the sheet, whereas GO-HGSs exhibits large wave length periodic ripples as well as buckling and kinks due to the hydrogen presence on single side of sheet. The wave length and magnitude of the ripples strongly depend on the hydrogen coverage.

The deformation in terms of ripples, kinks and buckling in these HGSs are mainly caused by the lattice mismatch between GA (GO/RGO) and GE strips. The bond length and lattice constant (the second-nearest-neighbor distance) of GE are 1.42 and 2.46 Å, respectively. Due to hydrogenation, it is found that the lattice parameter of the GA, GO and RGO sheets are increased by around 5%, which is in good agreements with previous studies [100, 106]. Hence, the hydrogenation induces interfacial strain between GA (GO/RGO) and GE strips, leading to the warping of the HGSs, a phenomenon similar to the warping of pure GE sheets induced by their compressive edge stress [107, 108].

Fig. 3.3. Periodic ripples form in GA-, GO- and RGO-HGSs with different width fractions f upon relaxation. Particularly, kinking and buckling are found in GO-HGSs as highlighted in the circles.

Mechanical and physical properties of a GE sheet strongly depend on its structure, particularly its morphology [109]. In practical applications, GE sheets are generally used in their flat form, which can be realized by subjecting them to external in-plane tensile loads. This study considers the thermal properties of HGSs only when they exhibit flat morphology. Therefore, before imposing the heat flux J to the HGSs, structural optimization is conducted to reduce or minimize the ripples or buckling by applying an equal biaxial stretching on their initial configurations which is constructed using the lattice parameter of GE. The critical stretching ratios at which all these HGSs at 300K begin to exhibit flat morphology are obtained to avoid excessive stretching effect. The

study shows that almost all these HGSs with different width fractions f can become flat when the biaxial stretching ratio R increases to around 1.05, a value that matches the lattice parameter increase in the GA (GO/GRO) sheets. Moreover, these HGSs stretched at this ratio are found to remain flat after the heat flux is imposed.

3.4. Thermal conductivity

The thermal conductivities λ of GE, GA, GO and RGO sheets are calculated, as listed in Table 3.1. The results of GE and GA sheets demonstrate consistency with those reported in the literature with minor deviations [110]. The minor difference may be caused by the deviations in calculating λ from the number of sample data collected, the number of iterations and the length of simulation time. It has been pointed out that the application of different heat fluxes would also lead to minor deviation in λ [81].

Table 3.1 Thermal conductivities λ (W/mK) of pure GE, GA, GO and RGO sheets

	Present results	Reported results [67]	λ/λ_0
GE	77.3	89.6	1.0
GA	33.2	28.8	0.43
GO	30.7	---	0.40
RGO	19.6	---	0.25

It is also necessary to note that the λ of GE sheets with dimensions of a few microns was experimentally measured to be in the range of 2500-5000W/mK [3, 111]. The GE sheets in the present model and reported models [63, 67] have dimensions no more than 20 nm and demonstrate about the same value of λ , which however is much smaller than

2500-5000W/mK due to the size effect at the nanoscale [63, 67, 112]. The length λ of the phonon MFP of GE that affects λ is about 770 nm, which means that the phonon paths in these modeled GE sheets would be cut off. According to the Debye equation, $\lambda = C_v v \lambda / 3$, the much lower λ obtained from the MD simulations is explainable.

For convenience, the λ of a GE sheet is denoted by λ_0 . The λ of the GA sheet is found to be 43% of λ_0 . Such a decrease is caused by the transformation of all the sp^2 bonds in the GE sheet to the sp^3 bonds in the GA sheet, because the thermal transport ability of the sp^3 bonds is lower than that of the sp^2 bonds [67, 68]. In contrast, the λ of the GO sheet is found to be 40% of λ_0 , which is slightly lower than that of the GA sheet, though only one half of the sp^2 bonds in the GE sheet are transformed into the sp^3 bonds in the GO sheet and these bonds are isolated by each other. In the RGO sheet, the numbers of sp^2 and sp^3 bonds equal to those of the GO sheet. However, the λ of the RGO sheet is only 25% of λ_0 and is 40% smaller than that of the GO sheet (refer to Table 3.1).

Previous studies have demonstrated that the thermal conductivity λ of nanostructures can also be affected by their internal strain [63, 66]. In this study, the λ of GA-, GO- and RGO-HGSs would also be affected by their internal strain due to the biaxial stretching applied to make them in the flat form. Nevertheless, since all the HGSs are under the same stretching ratio, the effect of the internal strain on λ is not quantitatively analyzed here. This study focuses on the effect of the hydrogenation style and hydrogen coverage on λ .

Figure 3.4 illustrates the effect of the hydrogen coverage f on λ of flat HGSs. The values of the λ in this figure are normalized with respect to λ_0 . The ratio λ/λ_0 of these

sheets for $f = 0$ is around 0.7 rather than 1, which is due to the 5% biaxial stretching applied. Similar reductions have previously been reported for single-layer GE and single-wall CNTs [113]. In the presence of hydrogenated strip in GE sheets, the λ further drops significantly in all these HGSs.

There is a sharp decrease in the λ when $f < 0.2$, and there onwards slight reduction observed for $0.2 < f < 0.8$. However, a slight increasing trend is observed when $0.8 < f$. The dramatic reduction can be attributed to the introduction of sp^3 bonds into the sheets with pure sp^2 bonds, which induces interfacial phonon scattering between the GE and GA/GO/RGO strips, while the increasing trend is due to the disappearance of these interfaces as well as approaching to uniform distribution of sp^3 (in GA-HGSs) or combination of sp^2 and sp^3 bonds (in GO-/RGO-HGSs) as f approaches 1.0. Moreover, RGO-HGSs always have the lowest value of λ among the three HGSs for any given f .

Fig. 3.4. Dependence of λ of GA-HGSs, GO-HGSs and RGO-HGSs on f .

3.5. Phonon spectrum analysis

To elucidate the underlying mechanism of the above phenomenon, a detailed analysis of the phonon spectra is conducted by performing the fast Fourier transform on the velocity auto-correlation function [114]:

$$P(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega t} \left\langle \sum_{j=1}^N v_j(t) v_j(0) \right\rangle d\omega \quad (3.1)$$

where ω and $v_j(t)$ denote the angular frequency and velocity of the atom j at time t , respectively. The ensemble average in the angular bracket is substituted by time averaging, which is performed over 50 ps after the realization of the equilibrium state. During the time averaging, the sample velocities are extracted from the simulation every 5 fs. The total spectra of GE, GO, RGO and GA sheets are presented in Fig. 3.5(a). It shows that hydrogenation in GO, RGO and GA sheets remarkably softens the G-band of the phonon spectra, which means the softening of the system and the reduction of the Debye temperature, thereby decreasing λ .

In addition to the G-band softening, the enhanced coupling effect between the in-plane and out-of-plane phonon modes of the hydrogenated GE sheets provides another explanation to their dramatic reduction in λ . In Fig. 3.5(b), the overlap of the in-plane and out-of-plane components of the power spectra, denoted by $S_{\text{in-out}}$, is calculated as [68, 115]

$$S = \frac{\int P_1(\omega) P_2(\omega) d\omega}{\int P_1(\omega) d\omega \int P_2(\omega) d\omega}, \quad (3.2)$$

where $P_1(\omega)$ and $P_2(\omega)$ are the powers of the in-plane and out-of-plane phonon spectra, respectively.

It is found that after hydrogenation, $S_{\text{in-out}}$ increases significantly from ~ 0.1 to ~ 0.5 , which indicates that the two phone modes are strongly coupled. Hence, the phonon scattering effect between them is greatly enhanced and reduces the thermal conductivity. Further study shows that the $S_{\text{in-out}}$ is closely related to the out-of-plane displacement of the C atoms. For the GE, GO, RGO and GA sheets, the averaged out-of-plane displacements of carbon atoms are found to be 0.09, 0.22, 0.31 and 0.80 Å, respectively, corresponding to their $S_{\text{in-out}}$ values of 0.11, 0.43, 0.44 and 0.49, which means the larger the out-of-plane displacement, the larger the $S_{\text{in-out}}$ would be.

Fig. 3.5. (a) Total phonon spectra of pure GE, GO, RGO and GA sheets, and (b) their in-plane (dash line) and out-of-plane (solid line) spectrum components, with $S_{\text{in-out}}$ denoting the overlap.

To explain why the thermal conductivity of RGO sheets is much lower than those of GO and GA sheets, the phonon spectra of the hydrogenated (sp^3 bonds) and unhydrogenated (sp^2 bonds) C atoms are calculated for both the GO and the RGO sheets (Fig. 3.6) and the overlap between these spectra, denoted by $S_{\text{CC-CH}}$, is also calculated, but with $P_1(\omega)$ and $P_2(\omega)$ denoting the spectra of the sp^2 bonded C atoms and sp^3 C atoms.

The fact that RGO sheets have much smaller S_{CC-CH} value than GO sheets indicates the scattering effect between the phonon modes of sp^3 and sp^2 bonds are more intensive in the RGO sheets, which further lowers their thermal conductivity, as compared to those of the GO and GA sheets. Moreover, the same phenomenon is found by analyzing the phonon spectra of GO and RGO strips inside the GO- and RGO-HGSs. Since the phonon spectra of GE strips in different HGSs are found to be almost the same, it is reasonable to attribute the lower thermal conductivity of RGO-HGSs to the more intensive phonon scattering effect between the sp^2 and sp^3 bonds in the RGO strip. The phonon spectra analysis reveals that the combined effect of the G-band softening, S_{in-out} and S_{CC-CH} reduces the thermal conductivity of GE significantly in the presence of hydrogenation.

Fig. 3.6. The phonon spectra of the carbon atoms with sp^2 (black solid line) and sp^3 bonds (red dot line) in GO and RGO sheets, with S_{CC-CH} denoting the overlap.

3.6. Summary

MD simulation is conducted to study the thermal conductivities of GA-HGSs, GO-HGSs and RGO-HGSs. The effect of hydrogenation patterns and hydrogen coverage f on their morphology and thermal conductivity is investigated. It shows that hydrogenation

can induce periodic ripples in these HGSs and even buckling in GO-HGSs. Simulation results reveal that the λ of the HGSs with flat morphology is 30% to 75% less than that of the pure GE sheets and such decrease depends on f . Moreover, among these HGSs, RGO-HGSs always have the lowest λ . Such phenomena are explained by conducting the phonon spectra analysis. It is found that the coupling effect of the in-plane and out-of-plane phonon modes in GE sheets is significantly enhanced by hydrogenation. The intensive phonon scattering effect between hydrogenated and unhydrogenated carbon atoms inside the RGO-HGSs is responsible for their low λ as compared to those of the GO-HGSs.

Chapter 4. Tuning the Thermal Conductivity of SE via Isotopic Doping

As one type of recently developed 2D nanostructures, SE shares similar lattice structure and electronic properties with GE, and therefore becomes another promising candidate in future nanodevices. However, it was reported that the 2D lattice structure of SE does not bring to it excellent thermal conduction properties as those of GE, but instead makes SE a low-thermal-conductivity material which has potential applications as good thermoelectric materials. This chapter investigates the thermal conductivity of SE and the effect of isotopic doping.

4.1. Application of SE as a thermoelectric material

Similar to GE, SE is also a single layer of silicon atoms arranged in a stable hexagonal lattice structure but with slight local buckling [18]. Due to its unique lattice structure, SE has band structures similar to those of GE and thus excellent electronic transport properties such as ultra-high Fermi velocities of 10^5 - 10^6 m/s [17, 19]. GE has high thermal conductivities of 3000-5000 W/m K [3]. In contrast, the recent MD studies showed that the in-plane thermal conductivity of SE at room temperature is in the range of 20-60 W/mK [65, 116-118], which is much lower than that of bulk Si (150-200 W/mK). With excellent electric properties and low thermal conductivity, SE would be promising as a thermoelectric material for next-generation power generators or refrigeration applications [55, 119].

Although thermoelectric materials have such advantages as high reliability, light weight and environmental benignancy, their low efficiency significantly limits their wide applications. The efficiency of thermoelectric materials can be characterized by the figure-of-merit $ZT = S^2 \sigma T / \lambda$, where S , σ and λ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively, and T is the absolute temperature [120]. A simple approach for efficiency improvement of ZT is to minimize the thermal conductivity λ or maximize the power factor $S^2 \sigma$ or both. To compete with the traditional energy conversion methods, the figure-of-merit should meet $ZT > 3$. However, up to now, even improved bulk materials have rarely realized $ZT > 1$ [121]. Therefore, nowadays research in this area has been directed towards nanoscale materials due to their large surface-to-volume ratio and explicit surface reconstruction effect.

A recent study based on the combination of the non-equilibrium Green's function method and MD simulation has demonstrated that SE nanoribbons (SNRs) can exhibit excellent thermoelectric performance [122]. This performance is achieved by reducing their width to suppress the thermal conductivity. However, narrow SNRs have low mechanical strength and structural stability and it is challenging to control their size distribution. Thus, it would be advantageous to develop approaches that reduce the thermal conductivity of SE but do not rely on its size.

4.2. Isotopic doping

Isotopic doping is an efficient method to tune the properties of nanomaterials just as hydrogenation. In this Chapter, doping means that the Si atoms in SE are substituted by their isotopes or other heteroatoms such as C, B and N. Isotopic doping method has

previously been used to modify the properties of GE. For example, a field-effect transistor consisting of a metal-semiconductor-metal junction can be constructed by selective doping of the GE nanoribbon edges with B or N atoms [123]. When GE is doped with Al atoms, the electronic structure of the C atoms can be altered, enhancing the hydrogen storage capacity of GE at room temperature [124]. Density functional computations have revealed that the introduction of appropriate dopants could drastically improve the sensitivity of GE-based chemical gas sensors [125].

In terms of the thermal properties, the MD simulation results show that, by isotopic doping, the thermal conductivity of GE monolayers and Si nanowires can be dramatically reduced even at a low doping percentage [126, 127]. Moreover, ultra-low thermal conductivity can be achieved if the dopants are arranged into a superlattice structure [127]. Isotope doping has such advantage that it would not affect the electronic properties of the nanostructures since all the isotopic atoms lie in the same position in the periodic table of elements and have the same electronic structure. This advantage provides the convenience to improve the thermoelectric properties of nanomaterials by solely adjusting the thermal conductivity without creating damage to their electronic properties.

In this chapter, the method of isotopic doping is adopted to tune the thermal conductivity of SE nanosheets. Two doping patterns are considered: random pattern and periodic pattern (or superlattice structure). The effects of the doping percentage, the length of the superlattice period and the roughness of the periodic interfaces will be investigated.

4.3. Simulation model

Figure 4.1 illustrates the model configuration of the zigzag and armchair oriented SE nanosheets (SNSs). Initially, all the Si atoms are placed in a honeycomb-lattice structure of which the in-plane atomic distance and lattice constant are set to be 2.30 and 3.98 Å, respectively, as reported from the experiments [17]. In addition, a small out-of-plane displacement $\delta = 0.44$ Å is applied to the Si atoms as shown in Fig. 4.1(c) to mimic the local buckling experimentally observed in SE. The periodic boundary condition is applied along the width (Y) direction, while the fixed boundaries are applied at the left and right ends of the SNSs, as denoted by the solid squares. The interactions of the Si-Si atoms are described by the SW potential with a recently developed parameterization set for the SE monolayer [86].

At first, the initial configuration is relaxed using the constant pressure and temperature (NPT) ensemble near $T = 300\text{K}$ for 50 ps with the time step $\Delta t = 0.5\text{fs}$. The SW potential with a recently developed parameterization set for the SE monolayer [86] is used to describe the Si-Si interactions. Upon the relaxation of the system, the simulation is conducted under the NVT ensemble for 50 ps to ensure that the system is in an equilibrium state. Afterwards, the system is switched to the NVE ensemble to keep the energy conserved. The atoms denoted by triangle symbols next to the two fixed boundaries are placed in two Nose-Hoover thermostats. The temperature of the left thermostats is set to be $T - \Delta T$; while that of the right thermostats is $T + \Delta T$. In the simulation, ΔT is kept as 50K.

The simulation is conducted for 5×10^6 steps to allow the system to reach a steady state, during which a stable temperature gradient ∇T can be established along the length

X direction. To maintain this temperature gradient, a small amount of heat $\Delta\xi$ is added into the right thermostat; while the same amount of energy is reduced from the left thermostat at each time step. As a result, the thermal conductivity λ can be obtained by $\lambda = -\Delta\xi/(A\Delta t\nabla T)$ as discussed in Section 3.2. In calculating the area A , the thickness of SNSs is taken as 3.14 Å which is the interlayer space of the (1 1 1) planes of Si.

Fig. 4.1. Schematic of (a) zigzag and (b) armchair oriented SNSs, and (c) the small local out-of-plane buckling.

4.4. Thermal conductivity of pristine SNSs

Since ^{28}Si has the highest natural abundance of 92%, compared with its isotopes ^{29}Si (5%) and ^{30}Si (3%). Besides these three, ^{42}Si and ^{43}Si are also observed. Here, the pristine SNSs are considered as consisting of only ^{28}Si atoms.

The thermal conductivity λ of pristine SNSs is calculated for various lengths. Figure 4.2 shows that the λ of both the armchair and zigzag oriented SNSs first dramatically increases with the length ($L < 60$ nm) and then get close to the value for infinitely long SNSs. This value is obtained to be 25.4 and 27.7 W/m K for armchair and zigzag SNSs, respectively.

Fig. 4.2. Dependence of the thermal conductivity λ on the length L of SNSs.

The results obtained demonstrate that SE has much lower thermal conductivity than bulk Si. Moreover, it is found that the λ of zigzag SNSs is about 10% larger than that of armchair SNSs, which implies that SE demonstrates chirality-dependence in thermal conduction. Such anisotropic thermal conducting behavior has also been reported for GE nanoribbons [104] and nanosheets [57], and can be interpreted by the length of path for phonon to pass [57]. For the same system length L , the phonon paths along the armchair and zigzag directions are $1.35L$ and $1.15L$, respectively. A longer path means more phonons scattering which would lead to a lower thermal conductivity.

4.5. Thermal conductivity of isotope-doped SNSs with random patterns

The effect of isotopic doping is studied by taking armchair orientated SNSs as examples. The length of the SNSs is taken as 41.4 nm. The same SW atomic potential is adopted to describe the interactions between ^{28}Si and the other isotopic elements, but they are assigned with different atomic masses. At first, the ^{28}Si atoms of the pristine SNSs are randomly replaced by the ^{29}Si or ^{30}Si atoms. Figure 4.3 shows the λ of ^{29}Si - and ^{30}Si -doped SNSs as a function of the doping percentage f . As f increases, λ first decreases and then increases. Similar trends have been observed in the doping studies of GE nanoribbons [122, 126], CNTs [128], and Si nanowires [127].

Fig. 4.3. Dependence of the thermal conductivity λ of SNSs on the random doping percentage f .

The minimum value of λ is reached around $f = 50\%$ and a reduction of about 20% is achieved for ^{30}Si doping. It is remarkable that λ changes dramatically at the two ends, i.e., when $f < 20\%$ and $f > 80\%$. Such changes can be explained by the localization mechanism of phonon modes [126]. For a small f , each doping atom can localize certain

phonon modes. Due to this localization, the dopants are unfavorable for thermal transport. As f increases, the number of these localized phonon modes increases, leading to a dramatic reduction in λ . However, as f increases, the dopants become close to each other and start to affect their neighbors, slowing down the increase of the localized modes and therefore the decrease in λ . When f increases beyond 50%, the ^{29}Si or ^{30}Si atoms become dominant with the ^{28}Si becoming the dopants. Therefore, as f further increases, the doping effect weakens, leading to a reverse trend in λ .

4.6. Thermal conductivity of isotope-doped SNSs with superlattices

Superlattice is a periodic structure constructed by two (or more) materials aligned next to each other. Typically, the thickness of one layer in this periodic structure is several nanometers. The superlattice structures of a semiconductor have recently attracted intensive research interest due to their potential in reducing the thermal conductivity [129-132]. In this study, isotopic-superlattice structured SNSs (IS-SNSs) are constructed by arranging ^{28}Si and ^{30}Si atomic periods alternatively along the X direction, as shown in Fig. 4.4. The lengths of the ^{28}Si and ^{30}Si periods are denoted by l_{28} and l_{30} , respectively, and set to equal each other, which gives the result of doping percentage $f = 50\%$.

The interfaces in the superlattice structure play an important role in the thermal conductivity [61]. To investigate the effect of interface roughness, the smooth interfaces of IS-SiNSs are roughened by randomly replacing half of the ^{28}Si (^{30}Si) atoms at the interfaces with the ^{30}Si (^{28}Si) atoms, as delineated in the rectangular box (Fig. 4.4). For the IS-SNSs with $l_p \leq 1.38$ nm which is the length of four zigzag chains, when the interfaces

are roughened, the IS-SNSs degenerate to be equivalent to the randomly doped SNSs. In other words, in order to preserve the superlattice structure in the roughened IS-SNSs, the periodic length l_p should be larger than 1.38 nm.

Fig. 4.4. (a) Schematic of the isotopic-superlattice structured SNSs. Rectangular boxes delineate smooth and rough interfaces, the latter of which is constructed by randomly replacing half of the ^{28}Si (^{30}Si) atoms at the interfaces by the ^{30}Si (^{28}Si) atoms. Detailed interface atomic structures of (b) smooth and (c) rough interfaces with the pink circles representing the Si^{28} atoms and the black circles the Si^{30} atoms.

Figure 4.5(a) shows the dependence of the thermal conductivity λ on the periodic length l_p for ^{30}Si -doped IS-SNSs with smooth and rough interfaces. It is noted that as l_p decreases, λ first decreases to its minimum value around $l_p = 2.76$ nm and then

increases. At this critical point, the λ of IS-SNSs with smooth and rough interfaces accounts for only 70% and 58% of that of the pristine SNSs, respectively. Similar non-monotonic dependence of λ on l_p has also been observed in several other superlattice structures, including the isotope-doped Si nanowires [127], Si/Ge superlattice [132] and GE/h-BN superlattice [133].

Fig. 4.5. Dependence of the thermal conductivity λ on the periodic length l_p for (a) ^{30}Si and (b) ^{42}Si -doped IS-SNSs with smooth and rough interfaces.

At any given l_p , the λ of IS-SNSs with rough interfaces is always lower than that of IS-SNSs with smooth interfaces. Moreover, when the ^{30}Si atoms in the former IS-SNSs are replaced with heavier isotopic atoms ^{42}Si , λ turns to decrease monotonically with l_p (Fig. 4.5(b)). It is noteworthy that ^{42}Si atoms are radioactive and may not be adoptable in real applications. However, they offer the advantages to study the mass effect on isotopic doping, which may provide guidance for studying the thermal properties of other isotope-doped superlattice structures.

4.7. Phonon spectrum analysis

The non-monotonic dependence of λ on l_p can be explained by two competing mechanisms governing heat conduction in SNSs, namely interface phonon scattering and phonon confinement effects. Firstly, the mechanism of interface phonon scattering is applied to demonstrate the reduction in λ as l_p decreases. The phonon spectra $P(\omega)$ of SNSs composed by single type of Si atoms (^{28}Si , ^{30}Si or ^{42}Si) are calculated by using Eq. (3.1) as presented in Chapter 3. Figure 4.6 shows the calculated phonon spectra.

It is observed that the highest frequency of the phonon modes decreases as the mass of Si atoms increases, indicating the softening of the system. As a result, phonon spectra mismatch arises between the ^{28}Si and ^{30}Si (or the ^{28}Si and ^{42}Si) periods in IS-SNSs, leading to incoherent phonon scattering at the periodic interfaces. This interface phonon scattering is the same as that between the hydrogenated and unhydrogenated GE strips as previously discussed in Chapter 3.

Fig. 4.6. Phonon spectra of SNSs composed of single types of Si atoms (^{28}Si , ^{30}Si or ^{42}Si).

As the periodic length of the superlattice structure decreases, the number of the interfaces increases. Thus, the phonons are more frequently and intensively scattered as they propagate along the heat flux direction, and their MFP is also significantly reduced. Hence, λ decreases as the periodic length decreases. When the interfaces of IS-SNSs are roughened, the transmission of phonons across the interfaces becomes more diffusive, i.e., the transmitted phonons are distributed in a more random pattern, which intensifies the interface phonon scattering effect and induces an additional resistance to in-plane transport, and thus further reduces λ .

Besides the interface phonon scattering effect, the spectrum mismatch between the ^{28}Si and ^{30}Si (or the ^{28}Si and ^{42}Si) periods also gives rise to the phonon confinement effect. Such effect has previously been observed in GE superlattice structures and found to be disadvantageous for thermal transport [69, 134].

Figure 4.7 shows the phonon spectra of the ^{28}Si , ^{30}Si and ^{40}Si periods in the IS-SNSs with different periodic lengths. For the IS-SNSs with large $l_p = 10.35$ nm, the maximum frequencies of the phonon modes in the ^{28}Si , ^{30}Si and ^{42}Si periods are 17.2, 16.7 and 14.8 THz, respectively (Figs. 4.7(a) and (c)).

Consequently, phonon modes with the frequency higher than 16.7 (or 14.8) THz would be confined in the ^{28}Si periods of the ^{30}Si -doped (or ^{42}Si -doped) IS-SNSs. If these modes are confined perfectly, no ^{30}Si or ^{42}Si atoms will be excited to vibrate at frequencies higher than 16.7 or 14.8 THz, and thus these modes will not contribute to the thermal transport. However, the confinement in real materials is not so ideal and the ^{30}Si or ^{42}Si atoms can be slightly excited at these high frequencies, especially for small periodic length, as indicated in Figs. 4.7(b) and (d).

When the periodic length $l_p = 1.38$ nm, phonon modes with frequencies higher than 16.7 and 14.8 THz appear in the phonon spectra of ^{30}Si and ^{42}Si periods, respectively, though the spectrum powers at these frequencies are weak. Hence, the confined modes are enabled to transfer heat from one period to another at small periodic lengths, resulting in the weakening of the confinement effect.

Fig. 4.7. Phonon spectra of ^{28}Si , ^{30}Si and ^{42}Si periods in the (a-b) ^{30}Si - and (c-d) ^{42}Si -doped IS-SNSs with smooth interfaces for large and small periodic lengths.

To investigate the dependence of the confinement effect on l_p , the overlap S between the phonon spectra of the neighboring periods in the IS-SiNSs is calculated using Eq. (3.2) in Chapter 3 with $P_1(\omega)$ and $P_2(\omega)$ being the phonon spectra powers of the ^{28}Si and ^{30}Si periods (or the ^{28}Si and ^{42}Si periods), respectively. The larger the overlap, the less the spectra mismatch between the superlattice periods would be and thus the weaker the phonon confinement effect would be.

Fig. 4.8. Dependence of the phonon spectra overlap S between the ^{28}Si and ^{30}Si or ^{28}Si and ^{42}Si periods on the periodic length l_p .

Figure 4.8 shows the dependence of S on l_p . It is noted that as l_p decreases, S increases monotonically, indicating a weakening phonon confinement effect. This observation is consistent with the fact that the interaction of the confined phonon modes in different superlattice periods increases as their length decreases [135]. It is noted that the decrease in l_p also leads to an enhanced phonon scattering effect by reducing the length of phonon MFP, and thus the scattering effect competes with the confinement effect in affecting the

thermal conductivity. In the range of $l_p \geq 2.76$ nm, the enhancement of interface scattering is dominant when l_p decreases, thus leading to the decrease of λ . However, for $l_p \leq 2.76$ nm, the weakening of phonon confinement becomes dominant as l_p decreases, and thus results in a reverse increase in λ . This competition mechanism gives rise to the non-monotonic dependence of λ on l_p . When the interfaces inside the ^{42}Si -doped IS-SNSs are roughened, the interface scattering effect is enhanced and overweighs the weakening of phonon confinement even for $l_p \leq 2.76$ nm, and thus leads to the continuous decrease of λ (Fig. 4.5(b)).

4.8. Summary

MD simulation is conducted to study the thermal conductivity λ of SNSs. Simulation results indicate that the λ of SNSs is around 25-30 W/mK and exhibits anisotropic behavior. Moreover, it is found that isotopic doping is efficient in reducing λ . When the SNSs are doped with ^{30}Si atoms at the percentage of 50%, a maximum reduction around 20% can be achieved. This reduction can further be increased to around 40% when the doping atoms are arranged in a superlattice structure. As the periodic length l_p of the superlattice structure decreases, the thermal conductivity changes non-monotonically. The λ reaches to a minimum value at the critical point $l_p = 2.76$ nm and then increases. However, when the interfaces in IS-SNSs are roughened, the non-monotonic dependence of λ on l_p can turn monotonic if heavy isotopic atoms are doped. Detailed analysis of the phonon spectra demonstrates that the competition mechanism between the interface

scattering and confinement effect of the phonon modes is responsible for these phenomena.

Chapter 5. Interfacial Thermal Transport of GE/SE Monolayer Heterostructures

In parallel to the study of individual 2D nanomaterials such as SE and GE, recent research efforts have been devoted to the composite nanomaterials obtained by integrating various kinds of these 2D nanomaterials. By designing the combining sequences or patterns, heterostructures with fascinating properties can be achieved. So far, several kinds of such heterostructures have been successfully synthesized and found to work exceptionally well in practice [45, 46, 136-139]. Thermal transport behaviors of these heterostructures, especially at their interfaces, play a pivotal role in determining their functional performance. In this chapter, the interfacial thermal transport of a hybrid GE/SE monolayer is investigated. The effects of the temperature, monolayer length, interface mismatch strain and heat flux magnitude on the interface thermal conductance are studied with their underlying mechanisms being explored.

5.1. GE/SE monolayer heterostructures

Recent studies have shown that hybrid systems consisting of GE and various other 2D materials introduce additional structural diversities to further enrich the property and application space of 2D materials, and at the same time provide an alternative to facilitate their fabrication and design processes. Various 2D GE-based nanocomposites have been theoretically predicted and experimentally synthesized, such as GE/hydrogenated GE [100, 140], GE/SE [42, 141], GE/MoS₂ [142-144], GE/*h*-BN [145, 146] and GE/graphitic ZnO [147].

For GE/SE heterostructures, the structural, electronic and optical properties of GE/SE bilayers were studied [141]. It was found that the doping carrier concentration of SE and GE could be modulated by changing their interfacial spacing, which led to the formation of tunable p-n junctions in their hybrid structure. The optical adsorption rate was also enhanced, in comparison with those of individual SE and GE monolayers. Hybrid GE/SE monolayer superlattices were also proposed theoretically [42], which might be observed by integrating such experimental techniques as chemical vapor deposition, photolithography and chemical masking. It was suggested that the properties of Dirac electrons in both GE and SE of these superlattices could be preserved, and with a proper choice of their geometrical parameters, it would be possible to engineer them to shift the Fermi level close to the Dirac points.

To take advantages of such GE/SE heterostructures in advanced nanodevices, their thermal transport behaviors should be understood. At the nanoscale, the Joule heating induced by electronic current can cause heat to be spatially localized, which may lead to thermal hot spots [148]. As the nanodevices are continuously further miniaturized, more heat needs to be dissipated and the hot spots will form more easily. The excessive amount of thermal energy within a nanodevice, if not dissipated efficiently, could affect its performance or even cause its eventual failure by nucleating defects [149]. This problem will become more pronounced for SE as it has much lower thermal conductivity than GE and even bulk Si.

Many studies have been conducted on the thermal transport behaviors of individual GE and SE. However, the thermal transport mechanisms in GE/SE heterostructures remain unclear; particularly, the interface thermal conductance between GE and SE is yet

to be understood. Hence, this chapter aims to investigate the interface thermal conductance and thermal rectification of a hybrid GE/SE monolayer via MD simulation. The effects of the system size and temperature, external strain and heat flux on the interface thermal conductance are investigated. A detailed phonon spectra analysis is conducted to understand the underlying mechanisms.

5.2. Simulation model

The in-plane atomic distance of SE (2.30 Å) is much larger than the bond length of GE (1.42 Å). This difference makes it difficult to construct a lattice-matched interface between GE and SE along the same chirality. Considering the fact that the lattice constant of GE (2.46 Å) is about 7% larger than the in-plane atomic distance of SE, it is possible to form an interface by connecting the zigzag edge of GE with the armchair edge of SE [42].

The atomic configuration of a hybrid GE/SE monolayer is shown in Fig. 5.1. One SE sheet with the length $2L$ is set in between two GE sheets with the length L . The armchair (zigzag) and zigzag (armchair) edges of GE (SE) are orientated along the length X and width Y directions, respectively. Initially, all the C and Si atoms are placed in a honeycomb-lattice structure with the lattice constant set to be 2.46 and 3.98 Å for GE and SE, respectively. To capture the buckling feature of SE, the Si atoms in the GE/SE monolayer are initially displaced in an out-of-plane mode with the buckling distance of 0.44 Å (Fig. 5.1(b)). The interface is established through elongating SE by ~7% along the Y direction to match the lattice of GE. The distance between the C and Si atoms at the interface is set as 1.80 Å, which is the Si-C bond length of SiC.

To calculate the interface thermal conductance of the GE/SE monolayer, a constant heat flux J is imposed into the system and then maintained for a number of time steps to develop a steady temperature profile. For a hybrid system consisting of interfaces, a temperature drop ΔT_{in} at the interface is usually developed, which gives a measurement of the interface thermal conductance or the Kapitza conductance as $G = J / \Delta T_{\text{in}}$.

Fig. 5.1. (a) Atomic structure of a hybrid GE/SE monolayer and (b) local buckling of SE.

The thermal conductivity λ of a layered structure can be calculated using a mixture rule-based expression $\lambda^{-1} = \sum f_i \lambda_i^{-1}$, where f_i and λ_i are the volume fraction and thermal conductivity of the i th component [150, 151]. Based on this expression, the thermal conductivity λ_{H} of the hybrid GE/SE monolayer can be calculated by the following equation with the interfaces taken into account [150]:

$$\lambda_{\text{H}}^{-1} = \frac{1}{2} \lambda_{\text{GE}}^{-1} + \frac{1}{2} \lambda_{\text{SE}}^{-1} + \frac{1}{2L} (G^{-1}) . \quad (5.1)$$

Here, λ_{GE} and λ_{SE} are the thermal conductivities of the GE and SE sheets, respectively, and can be calculated from Fourier's law $J = -\lambda \nabla T$, where ∇T denotes the temperature

gradient in the GE or SE sheet. The effect of the interface to the thermal transport of the hybrid GE/SE monolayer can be estimated by the ratio $r = (2GL)^{-1}/\lambda_H^{-1}$. Since the reciprocal of the thermal conductivity of a material is the thermal resistivity, r can be taken as the ratio of the effective thermal resistivity of the interface to that of the hybrid GE/SE monolayer. The larger the ratio r is, the more intensively the interface will impede the thermal transport in the hybrid monolayer.

To simplify the calculation of r , the temperature gradients ∇T in GE and SE are approximated by $-\Delta T_{\text{GE}}/L$ and $-\Delta T_{\text{SE}}/L$, respectively, where ΔT_{GE} and ΔT_{SE} are temperature drops developed in GE and SE along the heat flux direction, respectively. By simply replacing G with $J/\Delta T_{\text{In}}$, λ_{GE} with $JL/\Delta T_{\text{GE}}$, and λ_{SE} with $JL/\Delta T_{\text{SE}}$, the ratio r can be reduced to $r = \Delta T_{\text{In}}/(\Delta T_{\text{In}} + \Delta T_{\text{GE}} + \Delta T_{\text{SE}})$.

Periodic boundary conditions are applied along both the X and Y directions. The interactions of the C-C and C-Si atoms are described by the Tersoff potential. In this study, the Tersoff potential also utilizes an optimized set of parameters from Ref. [152] to provide a better representation of the lattice dynamic properties of GE. The interactions of the Si-Si atoms are described by the SW potential with a recently developed parameterization set for the SE monolayer [86]. The same simulation procedure as presented in Section 3.2 is adopted with $\Delta t = 0.5$ fs and $\Delta \xi = 10^{-4}$ eV. The only difference is that both the heat flux direction from SE to GE and that from GE to SE are considered. When J flows from SE to GE, it is denoted by J^+ ; while J^- denotes a reverse flow.

5.3. Interface thermal conductance

For an imposed heat flux J , the temperature distribution along the length direction of the hybrid GE/SE monolayer is exemplified by the case of $L = 17$ nm, as shown in Fig. 5.2. A dramatic temperature drop ΔT_{In} occurs at the GE/SE interface. In both GE and SE, the temperature distribution shows a linear pattern except at the middle region of SE where phonon scattering gives rise to certain nonlinearity. Compared to ΔT_{In} , ΔT_{GE} and ΔT_{SE} are small, and r reaches 70% for the case shown. This indicates that the interface is the dominant resistance for the thermal transport in the hybrid GE/SE monolayer, and thus increasing the interface thermal conductance is important for improving the thermal conduction ability of the hybrid monolayer.

Fig. 5.2. Typical temperature profile along the length direction of the GE/SE monolayer.

Figure 5.3 shows the dependence of thermal conductance G on the length L for both J^+ and J^- . It is found that G increases monotonically with L and reaches a saturated value of ~ 250 MW/m²K around $L = 40$ nm. In contrast, the thermal resistance ratio r

decreases with L , indicating that the dominating effect of the interface is weakened as the monolayer length increases. The G of the GE/SE interface has the magnitude of the same order as those of the interfaces of Si-based hybrid systems, such as CNT/Si (~ 300 MW/m²K) [60], Si/SiO₂ (~ 235 MW/m²K) [153] and Si/Ge (~ 330 MW/m²K) [154], but is one order of magnitude larger than those of multi-layered GE nanostructures such as the GE/phenolic resin interface (~ 20 MW/m²K) [59] and the GE/SiC interface (~ 50 MW/m²K) [155]. The high interface thermal conductance of the GE/SE monolayer is due to strong interfacial covalent bond, in comparison to the weak van der Waals forces between the interfaces of the multi-layered GE nanostructures.

Fig. 5.3. Dependence of the thermal conductance G on the length L for the heat fluxes J^+ and J^- .

The length dependence of the interface thermal conductance has also been observed in other hybrid systems [60, 153, 154]. Such dependence arises when the system has a small size, especially when it is smaller than the phonon MFP. As the system size increases, phonon modes with longer wavelengths are excited. These phonon modes can

easily transmit across the interface without inelastic scattering and thus make extra contribution to the interface thermal conduction.

To further understand the length dependence of the interface thermal conductance and the role of long wavelength phonons, the phonon spectra $P(\omega)$ of GE and SE are calculated using Eq. (3.1) and shown in Fig. 5.4(a). Since GE is highly anisotropic, its spectrum is further decomposed into in-plane and out-of-plane components as in Figs. 5.4(b) and (c).

Fig. 5.4. (a) Total phonon spectra of GE and SE, and the decomposition of the GE spectrum into (b) in-plane and (c) out-of-plane components.

It is observed that most of the overlaps between the phonon spectra of GE and SE are located in the low frequency range of 1-15 THz, and the out-of-plane components of the GE spectrum contributes mostly to these overlaps. A similar coupling phenomenon was also observed between the phonons in polymer and the low-frequency out-of-plane

phonons in GE, which was identified to be the most important channel for thermal transport across the interface between the polymer and GE [59].

When more long-wavelength phonons are excited due to the elongation of the system, more low-frequency phonons are available in GE to couple with the phonons in SE, thus resulting in a larger G . However, in the extremely low-frequency region ($< \sim 0.5\text{THz}$), the spectrum power of SE is weak, suggesting that fewer phonons are excited in this region. Hence, when the length further increases from $L = 40\text{ nm}$ (Fig. 5.3), the newly excited long-wavelength phonons have frequencies smaller than 0.5 THz and no enough number of phonons in SE are available for coupling. Consequently, G finally reaches a saturated value as L increases.

5.4. Interface thermal rectification

As shown in Fig. 5.3, the thermal conductance G is affected by the heat flux direction, and is larger when heat flows from SE to GE than that for the flow in a reverse direction, which indicates the existence of the thermal rectification at the interface. The existence of the interface thermal rectification can be explained by the asymmetry in the phonon transmission caused by the mismatch of phonon spectra across the interface [70, 156].

Figure 5.4 shows that GE has a much wider phonon frequency range than SE and can transmit higher frequency phonons. As a result, GE can accept most of the phonons originating from SE, while SE is not able to transmit the high-frequency phonons from GE. Nevertheless, these high-frequency phonons may be inelastically scattered into lower-frequency ones that can then be transmitted by SE. When the heat flux flows from

GE to SE, the average temperature of GE is higher than that of SE. Hence, more high-frequency phonons are excited in GE but cannot transmit across the interface without inelastic scattering. When the heat flux flows from SE to GE, the average temperature of SE is higher, and it has more high-frequency phonons excited which can easily transmit to GE. Therefore, G becomes asymmetric for the two opposite directions, leading to interface thermal rectification.

Here, the interface thermal rectification ratio R is defined as $R = [(G^+ - G^-)/G^-]$, where G^+ and G^- are the interface thermal conductance for the heat flux J^+ and J^- , respectively. Fig. 5.5 shows that R decreases monotonically with the length L and becomes almost negligible beyond $L = 40$ nm. At small $L \approx 4.3$ nm, R reaches as high as 44%, a value comparable to those found in several other GE-based hybrid nanostructures including GE/isotope-doped GE [114], GE/hydrogenated GE [70], and thickness-asymmetric multi-layered GE [157].

This effect of the hybrid monolayer length is due to the fact that more long-wavelength phonons are excited to contribute to the thermal conduction as the length increases. Such contribution is independent of the heat flux direction because the long-wavelength phonons can easily transmit across the interface without being scattered. Moreover, for a large system length, multi-phonon scattering inside the GE and SE begins to increase and reduces the impact of the interface. Therefore, the rectification R decreases with the length L . This length dependence of the interface thermal rectification is in agreement with those previously observed in a hybrid argon/krypton system [158], asymmetric GE nanoribbons [159] and CNT intramolecular junctions [160].

Fig. 5.5. Dependence of the thermal rectification R on the length L .

5.5. Temperature effect

Nanodevices usually work at high temperatures due to the existence of hot spots and their high heat densities. Therefore, the study of temperature effect on the interface thermal conductance is vital to understand the nanodevice performances. The system with the length $L=17$ nm is chosen as an example. Figure 5.6(a) shows that the interface thermal conductance G increases monotonically with the temperature T , a phenomenon that has also been observed for other hybrid systems such as CNT/Si [60], SiO₂/Si [153] and Si/Ge [154]. This temperature dependence is opposite to that of λ_{GE} and λ_{SE} as observed in individual GE or SE. Hence, it can be predicted that the ratio r of the thermal resistivity at the interface to that of the entire hybrid monolayer decreases with T , which is further validated from the simulation results as shown in Fig. 5.6(b).

When T increases up to 700 K, the ratios r for both J^+ and J^- still stay beyond 65%, indicating that the thermal resistance of the whole hybrid monolayer is dominated by the interface even at high temperatures. As a result, the thermal resistance of the entire hybrid monolayer decreases as T increases. This feature is advantageous for heat dissipation of GE/SE monolayers, particularly at high temperatures.

Fig. 5.6. Temperature dependence of (a) the interface thermal conductance G and (b) the thermal resistance ratio r for two heat flux directions.

The temperature dependence of the interface thermal conductance can be explained as follows. At low temperatures, fewer phonons, especially those with high frequencies are excited to participate in the thermal transport. As a consequence, the coupling between phonons across the interface is reduced, leading to a smaller G . As T increases, more high-frequency phonons are excited and make extra contribution to the thermal transport. Moreover, higher temperatures also bring about increased inelastic interface phonon scattering, leading to increases in both the anharmonicity of atomic interactions and the phonon transmission coefficients of interfaces. Hence, G becomes larger as T increases.

It is noted that under different temperatures, G^+ is always larger than G^- , implying that the interface thermal rectification R is preserved as T changes. Figure 5.7 shows that R decreases dramatically as T increases, and reduces to only $\sim 3\%$, which is almost negligible, when T is up to 700 K.

Fig. 5.7. Temperature dependence of the interface thermal rectification ratio R .

The effect of temperature on the interface thermal rectification is due to the increase of the Umklapp phonon scattering. As the temperature increases, the Umklapp scattering begins to dominate. Hence, when the heat flux flows from GE to SE, high-frequency phonons from GE are scattered into multiple low-frequency ones which can then transmit across the interface, thus resulting in the increase in G^- . However, the Umklapp scattering has no significant effect on G^+ since high-frequency phonons in SE can always transmit into GE due to the wider phonon frequency range of the latter one. Consequently, as T increases, G^- would get closer to G^+ , leading to the decrease of R .

5.6. Strain effect

Thermal transport behaviors of nanomaterials can be significantly modified by applying external strain [113]. Previous studies have shown that a tensile strain along the heat flux direction dramatically changes the thermal conductance of individual GE [99] or SE [65], as well as that of the interface between pristine GE and isotope-doped GE [156]. The study of the morphology of hybrid GE nanosheets in Chapter 3 also indicates the importance of considering the interface mismatch strain in studying the thermal properties of GE-based composite materials. In the GE/SE monolayer, SE is elongated by 7% along the interface direction to match the lattice of GE in a strain-free state. To study the strain effect, the monolayer is compressed along the interface direction until the tensile strain in SE is reduced to zero. As the in-plane tensile strain in SE reduces, G increases monotonically (Fig. 5.8(a)) and G^+ and G^- tend to get closer to each other, resulting in the decrease of R (Fig. 5.8(b)).

The effect of compression on the interface thermal conductance G and rectification R can be explained by the broadening of the phonon spectrum of SE as shown in Fig. 5.9. With initial tensile strain in SE reduces, its phonon spectrum slightly shifts towards high frequency. Moreover, the peak around 2 THz is broadened and split into two new peaks, giving rise to more phonons with frequencies in the range of 1-7 THz. Since the in-plane compression resistivity of GE is near zero, its phonon spectrum is not affected by the compression applied. Therefore, the mismatch between the phonon spectra of GE and SE, especially in the low frequency range, is reduced and phonons across the interfaces are better coupled, thus leading to a larger G and a smaller R .

Fig. 5.8. Dependence of (a) the interface thermal conductance G and (b) the interface thermal rectification R on the tensile strain in SE along the interface direction.

Fig. 5.9. Phonon spectra of Si atoms under different tensile strains remained in SE.

5.7. Heat flux effect

In the above-discussed simulation, the heat flux is kept constant as $J = 10.5 \text{ GW/m}^2$ by setting $\Delta\xi = 10^{-4} \text{ eV}$. In practical applications, the heat flux in nanodevices can change

under different working conditions. Thus, the effect of the heat flux J on the interface thermal conductance G should be investigated.

A critical value of $J = 42 \text{ GW/m}^2$ ($\Delta\xi = 4 \times 10^{-4} \text{ eV}$) is found, below which G is almost independent of J . When $J < 42 \text{ GW/m}^2$, the thermal transport in the hybrid GE/SE monolayer is mostly dominated by the Fourier heat conduction. However, when $J > 42 \text{ GW/m}^2$, low-frequency kinetic waves are found to be excited in SE and then transmitted to the entire hybrid monolayer. Similar kinetic waves were also observed in CNTs and GE nanoribbons under high heat flux conditions [161, 162], and it was proposed that such waves provide an additional channel for the non-Fourier heat conduction [162]. The critical value of the heat flux for hybrid monolayers is much smaller than those for CNTs ($\sim 250 \text{ GW/m}^2$) [162] and GE nanoribbons ($\sim 400 \text{ GW/m}^2$) [161].

Figure 5.10 shows the phonon spectra of GE and SE for the case of $J = 52.5 \text{ GW/m}^2$ to demonstrate the excitation of the low-frequency kinetic waves for $J > 42 \text{ GW/m}^2$. A sharp peak appears at 0.65 THz in both GE and SE spectra, and is found to originate from their out-of-plane components. The average out-of-plane displacements of all the C and Si atoms are also found to be significantly larger than those for $J < 42 \text{ GW/m}^2$.

The existence of kinetic waves in 2D nanomaterials and their contribution to the overall thermal transport is of great interest. Furthermore, the thermal conductance of hybrid GE/SE monolayers is much lower than those of CNTs and GE, and thus their low-frequency kinetic wave mechanism that provides an additional channel for the efficient non-Fourier heat conduction could be more critical for the thermal transport.

Fig. 5.10. (a) Total phonon spectra of GE and SE for $J = 52.5 \text{ GW/m}^2$ and (b-c) their out-of-plane components.

5.8. Summary

The interface thermal conductance G of hybrid GE/SE monolayers is studied. It is shown that G depends on the heat flux direction and is larger when the heat flows from SE to GE than in the reverse direction, indicating the existence of thermal rectification at the interface. Particular attention of the study is then given to the effects of the size and temperature of the system, the strain and the heat flux on the interface thermal conductance and the thermal rectification.

It is found that G increases with both the temperature and the monolayer length until it reaches a saturated value at a given temperature. At 300 K, the saturated value of $\sim 250 \text{ MW/m}^2\text{K}$ is obtained for G . In contrast, the interface thermal rectification R decreases when the temperature or the monolayer length increases. At small system lengths, R can reach as high as 44%, a value comparable to those found in several other GE-based nanostructures. The length dependences of G and R are explained by the excitation of

long-wavelength phonons; while the temperature dependences of G and R are attributed to the excitation of high-frequency phonons and the increase of Umklapp phonon scattering, respectively.

When the tensile strain in SE along the interface direction is released, G is significantly enhanced but R is dramatically reduced. This is due to the broadening of SE phonon spectrum, which results in the reduction of mismatch of the phonon spectra across the interface. With a small heat flux of $J < 42 \text{ GW/m}^2$, G is found to be independent of J and the thermal transport is mainly governed by the Fourier heat conduction. However, as J increases beyond 42 GW/m^2 , low-frequency kinetic waves are excited in the GE/SE monolayer, providing an extra channel for the non-Fourier heat conduction. This excitation is demonstrated by the analysis of phonon spectra.

Chapter 6. Interfacial Thermal Transport of SE/GE Bilayer Heterostructures

GE and SE can be combined along the in-plane direction through the covalent bonding to form a monolayer heterostructure, as discussed in Chapter 5. An SE/GE bilayer heterostructure can also be formed by stacking the SE and GE monolayers upon each other with interactions of weak van der Waals forces. This bilayer heterostructure fits well with the currently hot trend towards developing advanced van der Waals heterostructures.

6.1. SE/GE bilayer heterostructures

In parallel with the searching and studying of GE-like materials, another research field has recently emerged and attracted tremendous attentions [44]. It deals with van der Waals heterostructures and devices constructed by vertically stacking different 2D crystals on top of each other. The resulting stack represents an artificial material assembled in a chosen sequence with blocks defined with one-atomic-plane precision. Between different stack layers, atoms interact via weak van der Waals forces. By designing the stacking sequence, heterostructures with novel functionalities can be obtained. Recently, several kinds of such van der Waals heterostructures have been successfully investigated or synthesized [143, 163, 164].

In terms of heterostructures composed by GE and SE, recent first-principles calculations have demonstrated that a free-standing SE sheet on a single GE sheet or between two GE sheets can be stabilized at room temperature [141, 165-168]. Due to the

weak van der Waals interaction between SE and GE, the excellent electronic properties of both GE and SE are preserved [168]. Furthermore, novel electronic and optical properties can be induced in the SE/GE heterostructures [141].

So far, the thermal transport behaviors of the SE/GE heterostructure, particularly the thermal conductance across the interface between SE and GE remains unknown. As discussed in Chapter 5, at the nanoscale, the nanoelectronics face severe challenges from Joule heating induced by electronic current, which can potentially cause deterioration and even failure to materials and even failure. Moreover, the previous study of the thermal conductivity of the monolayer SE (as presented in Chapter 4) indicates that its thermal conductivity is less than 30 W/mK and much lower than that of bulk Si. The low thermal conductivity of SE makes the heat dissipation challenge in the SE/GE heterostructure more severe.

Previous studies have shown that the low thermal conductance at the interface of low-dimensional materials such as GE and CNTs with their substrates or surrounding matrices is a major limitation for effective thermal transport and heat dissipation [155, 169, 170]. For example, due to the low thermal conductance at the CNT/polymer interface, polymer-based composites with CNTs as reinforcing phases show only a modest increase of the thermal conductivity over that of pure polymer matrices [171], despite that CNT is an excellent thermal conductor.

To enhance the interfacial thermal conductance, surface engineering approaches including chemical functionalization [172, 173] and atomic intercalation [174] are usually adopted. In this Chapter, thermal conductance at the interface of an SE/GE bilayer heterostructure is studied. The effects of the temperature, interface coupling strength,

thermal transport direction and hydrogenation of GE are investigated and understood by the phonon spectra analyses. Different GE hydrogenation patterns and coverages are concerned.

6.2. Simulation model

To model the SE/GE bilayer heterostructure, the SE layer is deposited on the GE layer, as illustrated in Fig. 6.1. Since, the lattice constant of SE ($a_{\text{SE}} = 3.98 \text{ \AA}$) is around ~60% larger than that of GE ($a_{\text{GE}} = 2.46 \text{ \AA}$), the supercell of the SE/GE heterostructure consists of a 2×2 supercell of SE and a 3×3 supercell of GE, and is delineated by the red dotted line. Accordingly, the lattice constant of the heterostructure is taken as $a_{\text{GE/SE}} = (3a_{\text{GE}} + 2a_{\text{SE}})/2 = 7.67 \text{ \AA}$ with a small lattice mismatch of ~3.0% for both GE and SE. This lattice mismatch is close to that from the recent first-principles calculations of one SE layer sandwiched between two GE layers [167].

Fig. 6.1. Atomic structure of the SE/GE heterostructure: (a) top and (b) side views. The pink and green balls represent the C and Si atoms, respectively.

Reportedly, the packing patterns of GE and SE, which describe the relative in-plane position between them, have a negligible effect on the structural stability and physical properties of the SE/GE heterostructure [141]. Therefore, the packing pattern effect is not taken into account in this work. The interlayer distance D , defined as the average vertical Si-C distance along the out-of-plane z direction, is set to be 3.60 Å, according to the previous first-principles calculations [141, 168]. The in-plane dimensions of the heterostructure are set as 10.5×10 nm.

Periodic boundary conditions are applied along the in-plane X and Y directions to remove the edge effect, with the free-boundary condition along the out-of-plane direction. The interactions of C-C atoms and those of C-H atoms are modeled by the AIREBO potential, while the SW potential is used to describe the interactions of the Si-Si atoms. To model the weak van der Waals force between SE and GE, the LJ potential is adopted as follows:

$$V(r_{ij}) = 4\chi\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right]. \quad (6.1)$$

Here, χ is a scaling factor and can be used to tune the interaction strength. The parameters ϵ and σ are given as $\epsilon_{\text{Si-C}} = 8.909$ meV, $\sigma_{\text{Si-C}} = 3.326$ Å, $\epsilon_{\text{Si-H}} = 5.767$ meV and $\sigma_{\text{Si-H}} = 2.932$ Å, according to the universal force field developed by Rappe *et al.* [175]. The cutoff distance of the LJ potential is set to be 10 Å, a value that is about three times $\sigma_{\text{Si-C}} = 3.326$ Å.

The thermal relaxation simulation, which mimics the experimental pump-probe approach, is performed to calculate the interfacial thermal conductance G . At first, the

initial configuration of the SE/GE bilayer is equilibrated at $T = 300$ K under the NVT ensemble for 50 ps with a time step of 0.1 fs. Upon realization of the equilibrium state, a temperature difference ΔT between GE and SE is then constructed by rapidly increasing GE to $T + \Delta T$ through the velocity rescaling method, while keeping SE at T (Fig. 6.1(b)). To stabilize ΔT , the simulation is conducted for another 50 ps during which GE and SE are placed in two separate thermostats to remain at $T + \Delta T$ and T , respectively.

Afterwards, the system is switched to the NVE ensemble with the thermostats removed. In the absence of temperature control, the system is allowed to relax thermally and the temperature difference ΔT decays with the thermal energy transfers between GE and SE due to the weak van der Waals interactions between them. The decay or relaxation speed of the temperature difference reflects how fast the thermal energy transfers and thus how large the interface thermal conductance is. Define the temperature of GE as T_G and its initial value as T_{G0} , while the temperature of SE as T_S and its initial value as T_{S0} . Under the condition of energy conservation as imposed by the NVE ensemble, the following equation can be obtained:

$$\frac{d}{dt}[C_{GE}(T_G - T_{G0})] = -GA(T_G - T_S), \quad (6.2a)$$

$$\frac{d}{dt}[C_{SE}(T_S - T_{S0})] = -GA(T_S - T_G), \quad (6.2b)$$

where A is the interface area between GE and SE, and C_{GE} and C_{SE} are their constant volume heat capacities, respectively, and can be calculated by

$$C = 3Nk_B \int_0^\infty P(\omega) \left(\frac{\hbar\omega}{k_B T} \right)^2 \exp\left(\frac{\hbar\omega}{k_B T} \right) / \left(\exp\left(\frac{\hbar\omega}{k_B T} \right) - 1 \right)^2 d\omega. \quad (6.3)$$

Here, N denotes the number of atoms, k_B is the Boltzmann constant, h is the Planck constant, T is the temperature, and $P(\omega)$ is the phonon spectrum power at the frequency ω and can be calculated by Eq. (3.1).

It is assumed that heat capacities of GE and SE do not change significantly during the thermal relaxation process and can be regarded as constants, Eqs. 6.2 and 6.3 can be rewritten as

$$\frac{dT_G}{dt} = -\frac{GA}{C_{GE}}(T_G - T_S), \quad (6.4a)$$

$$\frac{dT_S}{dt} = -\frac{GA}{C_{SE}}(T_S - T_G). \quad (6.4b)$$

The substitution of Eq. (6.4a) into Eq. (6.4b) reaches

$$\frac{d^2T_G}{dt^2} + (\alpha + \beta)\frac{dT_G}{dt} = 0, \quad (6.5)$$

with $\alpha = GA/C_{GE}$ and $\beta = GA/C_{SE}$. Similarly, the substitution of Eq. (6.4b) into Eq. (6.4a) reaches

$$\frac{d^2T_S}{dt^2} + (\alpha + \beta)\frac{dT_S}{dt} = 0. \quad (6.6)$$

The subtraction of Eq. (6.6) from Eq. (6.5) gives

$$\frac{d^2(T_G - T_S)}{dt^2} + (\alpha + \beta)\frac{d(T_G - T_S)}{dt} = 0. \quad (6.7)$$

The solution of this linear second-order homogeneous differential equation with the initial conditions of $\Delta T = T_G - T_S = T_{G0} - T_{S0}$ at $t = 0$ and $\Delta T = T_G - T_S = 0$ at $t \rightarrow \infty$ is given as

$$\Delta T(t) = \Delta T(0) \exp\left(-\frac{t}{\tau}\right). \quad (6.8)$$

Here, $1/\tau = \alpha + \beta = GA(C_{GE}^{-1} + C_{SE}^{-1})$ is in the unit of time and called the thermal relaxation time, which is to be determined by the simulation. As a result, the interface thermal conductance can be calculated by

$$G = \frac{C_v}{A\tau}, \quad (6.9)$$

where C_v is the effective constant volume heat capacity of the bilayer system and equals $C_{GE}C_{SE}/(C_{GE} + C_{SE})$.

In the simulation, $\Delta T = 200$ K is found to be a proper temperature difference. If ΔT is too small, the thermal relaxation process will be extremely noisy, making it difficult to apply Eq. (6.9) to calculate the thermal relaxation time τ . On the other hand, if ΔT is too large, it will become difficult to determine the temperature dependence of the interfacial thermal conductance G . The same temperature difference of $\Delta T = 200$ K was adopted previously to study the interface thermal conductance between CNT and its surrounding matrix [170, 176].

6.3. Interface thermal conductance

Figure 6.2(a) shows the temperature evolutions for both GE and SE during the thermal relaxation at $T = 300$ K. As time passes, the temperature of GE decreases while that of SE increases, indicating heat transfer from GE to SE. Since GE and SE have different heat capacities per area, their bilayer does not equilibrate at their middle temperature of 400 K. The final equilibrium temperature of the SE/GE bilayer is closer to the initial temperature of GE than that of SE because GE has a larger heat capacity per area than SE. The simulation shows that when GE and SE are set at 500 and 300 K,

respectively, their bilayer eventually equilibrates at ~ 440 K. In contrast, if GE and SE are set at 300 and 500 K, respectively, the system reaches the equilibrium temperature of ~ 360 K.

Fig. 6.2. (a) Evolution of the temperatures of SE and GE, and (b) their difference during the thermal relaxation. The exponential fitting in (b) is performed to obtain the relaxation time τ .

As shown in Fig 6.2(b), the temperature difference ΔT between GE and SE exponentially decays, which agrees well with Eq. (6.8). Exponential fitting of the curve gives the relaxation time τ as 31.95 ps. Therefore, the dependence of ΔT on t is obtained to be $\Delta T(t) = \Delta T(0)\exp(-t/31.95)$. Use Eq. (6.9), the interfacial thermal conductance G of the SE/GE heterostructure at 300 K is calculated to be $11.74 \text{ MW/m}^2\text{K}$. Simulation is also conducted for the initial conditions $\Delta T(0) = 100 \text{ K}$ and $\Delta T(0) = 150 \text{ K}$. The simulation results show that large fluctuation occurs to the $\Delta T(t)$ curve when $\Delta T(0) = 100 \text{ K}$ and the fluctuation reduces when ΔT increases to 150 K. For $\Delta T(0) = 150 \text{ K}$, G is calculated as $11.28 \text{ MW/m}^2\text{K}$, which is close to that obtained for $\Delta T(0) = 200 \text{ K}$. The obtained G is on the same order of those found for several other

GE-based interfaces, e.g., 21 MW/m²K for the GE/resin interface[177] and 28 MW/m²K for the GE/Si interface [178].

6.4. Temperature and interface coupling strength effect

Nanoelectronic devices usually work at different temperature conditions. The dependence of the interfacial thermal conductance G on the temperature T is investigated for various scaling factors χ . The temperature difference is kept at $\Delta T(0) = 200$ K. The simulation shows that the interlayer distance D almost does not change with χ . Figure 6.3(a) indicates that G increases monotonically with both T and χ .

As T increases from 200 to 700 K, G is increased by three to four times. This temperature dependence of G is in good consistence with those found at the interfaces of GE/Cu [179] and CNT/SiO₂ [170], as well as that for the GE/SE monolayer interface as discussed in Chapter 5. According to Eq. (6.9), the interfacial thermal conductance G depends on the effective heat capacity C_v and the thermal relaxation time τ for a given interface area A . Figure 6.3(b) shows that τ decreases monotonically with T . As T increases from 200 to 700 K, the τ for $\chi = 1$ is reduced by 65% (which means 186% increase for G) and C_v increases by 25%. This means the change in the initial temperature T of the SE/GE heterostructure affects the interfacial thermal conductance mainly through changing the thermal relaxation time τ . The temperature dependence of G can be explained by the same mechanism as discussed in Section 5.5 and thus is not repeated here.

Fig. 6.3. Dependence of (a) the interfacial thermal conductance G and (b) thermal relaxation time τ on the temperature T for different values of χ .

The increase of the interfacial thermal conductance G with the interface coupling strength χ can be explained from two aspects: (1) the coupling between the phonons of GE and SE is enhanced, which directly increases the efficiency of the interfacial thermal transport; (2) the coupling between the in-plane and out-of-plane phonons in GE is strengthened, which indirectly facilitates the heat transfer from GE to SE, as explained as follows.

In free-standing GE, the in-plane and out-of-plane phonons are well decoupled [180]. Most of the in-plane phonons have frequencies beyond the overlap range of 1-17 THz (Fig 5.4) and cannot contribute to the heat transport. When SE is located on GE, its various symmetries (e.g., reflection, translation and rotation) are broken, and the vibrations of its C atoms are altered by the GE-SE interactions, especially at the sites where the C and Si atoms share the same in-plane coordinates. As a result, the C atoms at these sites serve as scattering centers for the in-plane phonons of GE, which leads to the coupling of in-plane and out-of-plane phonons. Part of the heat stored in the in-plane

phonons of GE can be transferred to the out-of-plane ones and then transmitted to SE. This increases the heat transfer between GE and SE and thus the interfacial thermal conductance.

6.5. Thermal transport direction effect

Nanoscale systems with structure asymmetry and lattice anharmonicity can be utilized as thermal rectifiers which are one kind of the most fundamental thermal devices to be realized experimentally [181, 182]. In a thermal rectifier, the heat transport depends on the direction and the thermal conductance is larger in one direction than in the reserve direction. To investigate the effect of thermal transport direction on the interfacial thermal conductance G of the SE/GE bilayer, the transport direction in Fig 6.1(b) is reversed by setting the temperature of SE at $T + \Delta T$ and that of GE at T . Due to the different atom densities per area for GE and SE, they equilibrate at a different temperature to that when heat transfers from GE to SE. For example, at 300 K, the SE and GE layers equilibrate at ~ 360 K instead of 440 K when heat transfers from SE to GE.

Figure 6.5 shows the interfacial thermal conductance G with the thermal transport from SE to GE (denoted as $G_{S \rightarrow G}$) and that with the thermal transport in the reverse direction (denoted as $G_{G \rightarrow S}$) at different temperatures T . It is found that $G_{S \rightarrow G}$ is much smaller than $G_{G \rightarrow S}$ at any given temperature. The thermal rectification ratio is defined as $R = (G_{G \rightarrow S} - G_{S \rightarrow G}) / G_{S \rightarrow G}$. At $T = 300\text{K}$, $G_{S \rightarrow G}$ equals $9.52 \text{ MW/m}^2\text{K}$ which is only $\sim 80\%$ of $G_{G \rightarrow S}$, leading to $R \approx 0.23$. This rectification ratio is comparable to

those found in several GE-based nanostructures, such as the GE nanoribbons with asymmetric isotope doping [156].

Fig. 6.4. Interface thermal conductance G with the thermal transport from GE to SE and from SE to GE at various temperatures T .

The thermal rectification in the SE/GE bilayer is mainly because of two reasons: (1) different temperature dependences of SE and GE for the heat capacity and (2) different atom densities per area of SE and GE.

As the temperature T increases, more phonons are excited in both GE and SE. These newly excited phonons not only participate in the interface thermal transport but also lead to increase in the heat capacities of the SE and GE layers. As T increases from 300 to 500 K, the heat capacity C_{GE} of the GE layer increases by $\sim 20\%$, while the C_{SE} of the SE layer increases only by $\sim 3.5\%$. This indicates that more phonons are available for interface coupling in the case where the GE layer is increased to 500 K with SE being set at 300 K than the case where SE is increased to 500 K with GE set at 300 K. Although most of the

newly excited phonons in GE have high frequencies and do not directly participate in the interface heat transport, they can be scattered into multi low-frequency ones and then coupled with the phonons in SE due to the enhanced Umklapp scattering at high temperatures.

The atom density per area of the GE layer is 2.25 times larger than that of the SE layer. During the temperature increase, the larger atom density per area of the GE layer also brings about more phonon excitation to contribute to the interface thermal transport. Therefore, the interface thermal conductance G is larger when heat transfers from GE to SE than in a reverse transfer direction, leading to the thermal rectification effect.

It should be noted that the thermal rectification mechanism in the SE/GE bilayer is different from that in the hybrid GE/SE monolayer as in Chapter 5. This is because in the GE/SE monolayer, the GE and SE monolayer are connected with strong in-plane covalent bonds. The occurrence of thermal rectification in the monolayer is mainly due to the mismatch of phonon spectra across the interface, i.e., dramatic inelastic scattering of the high frequency phonon modes from GE at the interface when they transmit to the SE side. However, in the present SE/GE bilayer system, the SE and GE layers interact with each other through weak van der Waals force and thermal transport across the interface is mainly through the coupling of the low-frequency out-of-plane phonons. Thus, the mismatch of phonon spectra plays less role in leading to the thermal rectification effect.

6.6. GE hydrogenation effect

In this section, the effect of hydrogenation of GE on the interface thermal conductance G is investigated. As discussed in Chapter 3, there are two typical types of

hydrogenated GE (HGE): double-side HGE (DHGE) and single-side HGE (SHGE) as shown in Figs. 3.1(b) and (c), respectively. Both patterns are utilized to construct SE/DHGE and SE/SHGE heterostructures here.

Figure 6.5(a) shows the atomic configuration of the SE/DHGE heterostructure. In real application, the hydrogen coverage f of the SE/DHGE may not be full. Here, a partial hydrogen coverage is obtained by randomly removing the same number of H atoms on both sides of DHGE; that is to say, a random distribution pattern of the H atoms is considered. Thus, the present study focuses on the coverage ratio of the H atoms rather than the details of their distributions, although the latter might also affect the interfacial thermal conductance. The hydrogen coverage is defined as $f = N_1 / N_0$, where N_0 denotes half the number of the total C atoms in GE and N_1 denotes the number of the H atoms on one side.

To obtain the SHGE with the same hydrogen coverage f , all the hydrogen atoms on one side of the DHGE with the coverage f is removed. As shown in Figs. 5(b) and (c), according to the position of the H atoms on GE, the SE/SHGE heterostructure is further classified into two types: SE/THGE (top side) and SE/BHGE (bottom side). It is worth pointing out that after hydrogenation, the interlayer distance D increases slightly with the hydrogen coverage f , especially when the H atoms are located at the SE/GE interface. At $f = 100\%$, D equals 4.12, 4.02 and 3.70 Å for SE/DHGE, SE/THGE and SE/BHGE, respectively.

Fig. 6.5. Atomic configurations of (a) SE/DHGE, (b) SE/THGE and (c) SE/BHGE.

Figure 6.6 shows the dependence of the interfacial thermal conductance $G_{G \rightarrow S}$ on the hydrogen coverage f for all the three types of SE/HGE heterostructures. Since similar trends are found for $G_{S \rightarrow G}$, only the results for $G_{G \rightarrow S}$ is presented here and the general term G is used in the following discussion for simplicity. It is found that for both SE/THGE and SE/DHGE that have the H atoms at the SE/GE interface, G dramatically increases as f increases up to $f = 50\%$ and then decreases.

In contrast, for SE/BHGE that does not have interfacial H atoms, G first decreases and then slightly increases after $f > 10\%$. Overall, the change of G for SE/BHGE is almost negligible as compared to those for both SE/THGE and SE/DHGE. This indicates that hydrogenation is more efficient in tuning G when the H atoms are located between SE and GE. The maximum values of G for SE/THGE and SE/DHGE are 61.75 and 39.14 MW/m²K, respectively, which are three to five times higher than that of the pristine SE/GE heterostructure.

Fig. 6.6. Dependence of interfacial thermal conductance G on the hydrogen coverage f for three types of SE/THGE heterostructures.

For SE/HGE heterostructures, their thermal transport across the interface through both the interaction of the Si-H atoms and that of the Si-C atoms. To illustrate the contribution of the Si-H interaction, the van der Waals interaction of Si-C atoms is turned off by setting $\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} = 0$. Alternatively, to illustrate the Si-C interaction, the van der Waals interaction of Si-H atoms is turned off by setting $\varepsilon_{\text{Si-H}} = 0$ and $\varepsilon_{\text{Si-C}} \neq 0$. For both assumed scenarios, the interfacial thermal conductance G for the SE/THGE with $\chi = 1$ is calculated for various hydrogen coverages f , as shown in Fig. 6.7. For comparison, the results for the scenario that considers full interactions ($\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} \neq 0$) are presented as well.

When $\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} = 0$, G increases with f until $f \approx 50\%$ and then decreases afterwards. This non-monotonic dependence is related to two mechanisms. On the one hand, as f increases, more H atoms participate to interact with Si atoms and thus enhance

the interface thermal transport. On the other hand, H atoms have a small atomic mass and tend to vibrate at high frequencies.

Fig. 6.7. Interfacial thermal conductance G of SE/THGE versus its hydrogen coverage f for different atomic interaction conditions.

Figure 6.8 presents the phonon spectra of the H atoms in the low-frequency range for three different hydrogen coverages. It shows that as f increases, the phonon spectrum shifts towards the high-frequency direction, and the spectrum power also dramatically decreases particularly in the range of 15-20 THz. As a result, the coupling between the phonons of the H atoms and those of the Si atoms is weakened, resulting in the reduction of the interface thermal transport. The two mechanisms compete to determine the interfacial thermal conductance G . When f is small, the former mechanism is dominant; when f is large, the latter one becomes dominant, thus resulting in a non-monotonic dependence of G on f .

Fig. 6.8. Phonon spectra of H atoms in the low-frequency range for three different hydrogen coverages f .

When $\varepsilon_{\text{Si-H}} = 0$ and $\varepsilon_{\text{Si-C}} \neq 0$, G increases with f upon $f \approx 50\%$ and then stabilizes. This increase of G is due to the enhanced coupling between the in-plane and out-of-plane phonons of C atoms. Figure 6.9 plots the in-plane and out-of-plane components of the phonon spectra for the C atoms in THGE. It shows that as f increases from 25% to 50%, the overlap between the in-plane and out-of-plane spectrum components dramatically increases, particularly in the frequency range of 15-30 THz. This results in an enhanced coupling between the in-plane and out-of-plane phonons, which can facilitate the heat transfer from THGE to SE. When $f > 50\%$, the overlap does not change much, thus leading to that G almost remains the same.

When $\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} \neq 0$, the interfacial thermal conductance G of SE/THGE changes with the hydrogen coverage f in the same manner as that for $\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} = 0$. A similar phenomenon is observed for SE/DHGE. This indicates that hydrogenation affects G of SE/HGE mainly through the Si-H interaction.

Fig. 6.9. In-plane and out-of-plane components of the phonon spectra for the C atoms in THGE for two different hydrogen coverages.

Figure 6.7 also shows that the interfacial thermal conductance G of SE/THGE with full interactions being taken into account ($\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} \neq 0$) is approximately the summation of G with only Si-C interactions ($\varepsilon_{\text{Si-H}} = 0$ and $\varepsilon_{\text{Si-C}} \neq 0$) and G with only Si-H interactions ($\varepsilon_{\text{Si-H}} \neq 0$ and $\varepsilon_{\text{Si-C}} = 0$). It implies that the effect of Si-H interactions on the thermal transport across the SE/HGE interface is decoupled with that of the Si-C interactions.

Besides the hydrogen coverage f , the hydrogenation pattern can also significantly affect the interfacial thermal conductance G of SE/HGE. The G of SE/DHGE always lies between those of SE/THGE and SE/BHGE, regardless of f (Fig. 6.6). This effect is caused mainly by the change in the average vertical distance $d_{\text{Si-H}}$ for the Si-H atoms along the out-of-plane direction due to different hydrogenation patterns.

When H atoms are bonded to C atoms in GE, the latter ones are pulled away from their initial positions with an out-of-plane displacement of ~ 0.25 Å along the Z direction. Such displacement is positive when H atoms are located on the top side of GE, but negative when H atoms are on the bottom side. As a result, for SE/THGE, the Si-H atoms have $d_{\text{Si-H}} = 4.02 - 1.10 - 0.25 = 2.67$ Å, which is much smaller than the $d_{\text{Si-H}} = 3.70 + 1.10 + 0.25 = 5.05$ Å for SE/BHGE. With a larger $d_{\text{Si-H}}$, the van der Waals interaction of the Si-H atoms becomes weaker. Considering the fact that the Si-H interaction plays a dominant role in determining the interfacial thermal conductance G of SE/HGE as demonstrated above, the G of SE/THGE is much larger than that of SE/BHGE. In addition, due to the large $d_{\text{Si-H}}$ for SE/BHGE, the interaction of the Si-H atoms is very weak and contributes little to the interface thermal transport. As a result, the G of SE/BHGE is almost independent of the hydrogen coverage f (Fig. 6.7).

In SE/DHGE, the H atoms on the top side of GE is much closer to the Si atoms than those on the bottom side, and thus contribute most to the interface thermal transport. These top H atoms have the average Si-H distance of $d_{\text{Si-H}} = 4.12 - 1.10 - 0.25 = 2.77$ Å, a value that is slightly larger than the $d_{\text{Si-H}} = 2.67$ for SE/THGE. Moreover, the interlayer distance of $D = 4.12$ Å for SE/DHGE is also larger than the $D = 4.02$ Å for SE/THGE. Therefore, both the Si-H and the Si-C interactions are weaker for SE/DHGE, leading to that it has a smaller G than SE/THGE.

More importantly, due to double-side hydrogenation, DHGE has two times larger number of H atoms than THGE for the same hydrogen coverage. As a result, more phonons have high frequencies in DHGE, and the coupling between the phonons of H

atoms and those of Si atoms in SE/DHGE becomes weaker than that in SE/THGE, as indicated in Fig. 6.8. This weakening effect is also responsible for the lower G of SE/DHGE than that of SE/THGE.

6.7. Summary

The interfacial thermal conductance G of an SE/GE heterostructure is studied. The effect of the temperature, interface coupling strength, thermal transport direction and GE hydrogenation is investigated. The G of pristine SE/GE heterostructures at room temperature is calculated as $11.74 \text{ MW/m}^2\text{K}$ when the heat transfers from GE to SE, and is $9.52 \text{ MW/m}^2\text{K}$ when from SE to GE, showing a high thermal rectification ratio.

Furthermore, it is found that G increases monotonically with both the temperature and the interface coupling strength. As the interface coupling strength increases, not only is the coupling between the phonons of GE and SE enhanced, but also the coupling between the in-plane and out-of-plane phonons in GE is strengthened, which both facilitate the heat transfer from GE to SE and thus bring about the increase of G .

Double-side and single-side hydrogenation patterns are used to construct the SE/DHGE and SE/SHGE (including SE/THGE with H atoms on the top side of GE and SE/BHGE with H atoms on the bottom side) heterostructures, respectively. It is found that SE/DHGE and SE/THGE have much larger interfacial thermal conductance than pristine SE/GE, and SE/THGE has the largest value. However, hydrogenation almost has no effect on the interfacial thermal conductance of SE/BHGE. Furthermore, it is found that as the hydrogen coverage f increases, G first increases and then decreases for both SE/DHGE and SE/THGE, but remains almost unchanged for SE/BHGE. At $f \approx 50\%$, a maximum G

of $61.75 \text{ MW/m}^2\text{K}$ is obtained for SE/THGE, which is about five times larger than that of pristine SE/GE. These phenomena are well explained by the interactions of the Si-H atoms and those of the Si-C atoms.

Chapter 7. Thermal Transport of GE/MoS₂ Bilayer Heterostructures

The availability of various types of two-dimensional materials, such as GE, SE and MoS₂, provides a fertile ground for the design and fabrication of the novel van der Waals heterostructures. Different from the SE/GE bilayer heterostructure which is still in their theoretical stage, the GE/MoS₂ bilayer heterostructure has already been successfully synthesized and proved to work well in practical applications. In this chapter, the thermal transport in the GE/MoS₂ bilayer heterostructure is studied. Both the in-plane thermal conductivity and the out-of-plane interfacial thermal conductance are investigated.

7.1. GE/MoS₂ bilayer heterostructures

Nanoelectronic devices using 2D materials as building blocks offer many benefits for further miniaturization beyond Moore's law and are promising for extending electronics into new application domains. In particular, with their excellent mechanical flexibility and transport properties, 2D materials have attracted great interest in the realization of transparent and flexible electronic systems.

It is well known that the intrinsic zero-band gap of GE imposes great challenges for its application as novel nanoelectronics. Although various methods including strain engineering, chemical functionalization and doping have been proposed to tune the band gap of GE, intensive efforts are still needed for the realization of these methods during its real applications. Monolayer MoS₂, on the contrast, is a direct band gap semiconductor and thus is very interesting as a material complementary to GE.

Recently, it has been found that the integration of GE and MoS₂ monolayers into a hybrid heterostructure offers the possibility to create devices with various functionalities [45, 46, 85, 136-139, 183, 184]. Electronic logic and memory devices have been experimentally constructed based on GE/MoS₂ hybrids [45, 46, 136, 137]. Hybrid GE/MoS₂ materials with excellent electrochemical performances have also been synthesized for the application of electrodes in lithium batteries [138, 139]. As the hybrid GE/MoS₂ structures are attracting more and more interest, their performances are limited by the same heat dissipation capabilities during operation as discussed for the SE/GE bilayer structure. The previous studies have demonstrated that the thermal conductivity of MoS₂ monolayer falls into the range of 1-35 W/mK [85, 183, 184], which is even lower than that of SE. Hence, the heat dissipation challenge in the GE/MoS₂ bilayer structure can be even more severe and thus should be studied.

7.2. Simulation model

The lattice constant for MoS₂ is $a_M = 3.12 \text{ \AA}$, which is ~25% larger than that of GE ($a_{GE} = 2.46 \text{ \AA}$). The GE/MoS₂ bilayer heterostructure is modeled in a similar way as the SE/GE bilayer, i.e., the GE layer is deposited on the MoS₂ layer, as illustrated in Fig. 7.1. The supercell of the GE/MoS₂ heterostructure, which is delineated by the red dotted line, consists of a 4×4 supercell of MoS₂ and a 5×5 supercell of GE. The lattice constant of the heterostructure is taken as $a_{G/M} = (5a_{GE} + 4a_M) / 2 = 12.39 \text{ \AA}$. The interlayer distance D that is defined as the nearest C-S distance along the out-of-plane Z direction is set to be $3.32 \text{ \AA}$, according to the previous first-principles calculations [144, 185].

Fig. 7.1. Atomic configurations of the GE/MoS₂ heterostructure: (a) top view and (b) side view.

Periodic boundary conditions are applied along the in-plane X and Y directions to remove the edge effect, with the free-boundary condition along the out-of-plane Z direction. The AIREBO potential is adopted to model the interactions of C-C atoms. The SW potential with a recently developed parameterization set for the MoS₂ monolayer [85] is used to describe the atomic interactions within MoS₂. This parameterization set has proved to be able to well reproduce the mechanical and thermal properties of MoS₂. To model the weak van der Waals force between GE and MoS₂, the LJ potential is adopted and the same scale parameter χ as in Eq. (6.1) is also adopted to tune the interface coupling strength. The parameters ε and σ are given as $\varepsilon_{S-C} = 7.355$ meV, $\sigma_{S-C} = 3.219$ Å, $\varepsilon_{Mo-C} = 3.325$ meV and $\sigma_{Mo-C} = 2.818$ Å. The cutoff distance of the LJ potential is set to be 10 Å, a value that is about three times $\sigma_{S-C} = 3.219$ Å. For the default interface interaction strength, the scaling factor is set as $\chi = 1$.

Figure 7.2 illustrates the configuration to calculate the in-plane thermal conductivity. The length of the bilayer system is set as $2L$, while its width is fixed at ~ 5 nm. Previous studies have shown that the thermal conductivities of GE and MoS₂ monolayers are not dependent on the width when it is larger than 3 nm.

Fig. 7.2. Schematic for calculating the in-plane thermal conductivity of the GE/MoS₂ bilayer.

The same simulation procedures as presented in Sections 3.2 and 6.2 are adopted to calculate the in-plane thermal conductivity and the out-of-plane interface thermal conductance, respectively. In the calculation of the heat flux J by $J = \Delta \xi / (2A\Delta t)$ for the in-plane thermal conductivity, the value of cross-section area A for the bilayer is denoted as A_B , while A_G for the GE layer and A_M for the MoS₂ layer. In the calculation of A , the thickness of the GE and MoS₂ layers are taken as $t_G = 3.44$ and $t_M = 6.09$ Å, respectively, and the thickness of the bilayer is taken as $t_B = t_G + t_M$.

While in the thermal relaxation simulation, the temperature of MoS₂ is set to be higher ($T + \Delta T$) than that of GE (T). This is because in practical applications, due to its high in-plane thermal conductivity, GE is adopted as the primary channel for heat

dissipation from GE-based nonodevices to their surrounding environment. Therefore, the thermal transport from MoS₂ to GE is of more interest than that along the reverse direction.

7.3. In-plane thermal conductivity

7.3.1. Thermal conductivity at the nanoscale length

Figure 7.3(a) shows the temperature distribution along the X direction of the GE/MoS₂ bilayer for the case of $L = 19.4$ nm after a stable temperature gradient is imposed. Since the system is symmetric about the hot region, only the temperature distribution of the left half system is shown. The temperature distributions of constituent GE and MoS₂ layers are also presented for comparison. It is found that the temperature distribution of the heterostructure bilayer lies between those of the individual GE and MoS₂ layers. In both GE and MoS₂, the temperature distribution shows a linear pattern except near the hot and cold regions where phonon scattering gives rise to certain nonlinearity. Linear fitting shows that the temperature gradients ∇T for GE, MoS₂ and the bilayer are 0.336, 0.426 and 0.378 K/Å, respectively.

Figure 7.3(b) shows that the energy added in or subtracted from the hot and cold regions is a linear function of time. The linear slopes give the heat fluxes J that flow across the GE and MoS₂ layers, based on the formula $J = \Delta\xi/(2A\Delta t)$. The heat flux J_G for the GE layer is obtained as 2.94×10^{11} J/m²s which is more than 10 times larger than the $J_M = 2.31 \times 10^{10}$ J/m²s for the MoS₂ layer, while the heat flux J_B for the bilayer is 1.20×10^{11} J/m²s. Therefore, the thermal conductivities λ of the GE/MoS₂ bilayer, the

constituent GE and MoS₂ layers are calculated as $\lambda_B = 31.74$, $\lambda_G = 87.50$ and $\lambda_M = 5.42$ W/m K, respectively.

Fig. 7.3. (a) Temperature distributions of the GE monolayer, MoS₂ monolayer and GE/MoS₂ bilayer; (b) energy added to or subtracted from the hot and cold regions as the function of time.

To validate the simulation results, the thermal conductivities of isolated GE and MoS₂ monolayers that have the same in-plane dimensions as the GE/MoS₂ bilayer are also calculated, which are 90.87 and 5.48 W/m K, respectively. The obtained thermal conductivity of 5.48 W/m K for isolated MoS₂ monolayer agrees well with previous reported value of 5.8 W/m K for the same system length and potential function used [85]. This value is also in good agreement of recent experimental measurement of ~ 0.25 -3.0 W/mK [186]. For the isolated GE monolayer, the obtained thermal conductivity of 90.87 W/m K is also close to those reported for GE monolayers with similar sizes by using either the AIREBO or potential [67, 187] the second-generation REBO potential [188].

The GE layer in the GE/MoS₂ bilayer has almost the same thermal conductivity as the isolated GE monolayer. Such phenomenon has also been reported for the GE bilayer [4, 189]. However, when a layer of GE was deposited on a silica or metal substrate, its

thermal conductivity was significantly suppressed due to its strong interaction with the substrate [190-192].

The MoS₂ and the GE layer have a negligible effect on the thermal conductivity of each other because of weak van der Waals interaction between them. However, the van der Waals interaction can be strengthened by various methods such as chemical functionalization and surface roughness modification. For example, when the GE surface is functionalized with specie that can have stronger interactions with S or Mo atoms, the interaction between the GE and MoS₂ layers will increase.

In the simulation, the change of the van der Waals interaction is realized by varying the interaction strength scaling factor χ (see Eq. (6.1)). Figure 7.4 shows the dependences of the normalized thermal conductivities of the GE/MoS₂ bilayer, the constituent GE and MoS₂ layers on χ . As χ increases, λ_B , λ_G and λ_M decrease monotonically and λ_M decreases more dramatically than λ_B and λ_G . When χ increases by 10 times, λ_M reduces by less than 15%. Since χ generally increases less than 5 times in practical applications [193], the in-plane thermal transport properties of the GE/MoS₂ bilayer, the constituent GE and MoS₂ layers can be well preserved when the interface interaction is strengthened.

The decrease of the in-plane thermal conductivity λ_G of the GE layer with the increasing interface interaction strength scaling factor χ can be explained by the enhanced coupling between the in-plane and out-of-plane phonons as discussed in Section 6.4. The interactions between MoS₂ and GE layers enhance the phonon-phonon scattering inside

them and thus reduce their thermal conductivity. Therefore, the λ_B of the entire bilayer decreases as its interface interaction strength increases.

Fig. 7.4. Dependence of λ on χ for the GE/MoS₂ bilayer, the constituent GE and MoS₂ layers. The values of λ are normalized by its values at $\chi=1$.

7.3.2. Thermal conductivity at the microscale length

Experimentally, the synthesized GE/MoS₂ bilayer tends to have an in-plane size ranging from dozens of nanometers to several micrometers. Currently, it is still challenging to conduct MD simulation for samples at the micrometer scale. Hence, an approximation approach is developed in this section to predict the thermal conductivity of GE/MoS₂ bilayers at the microscale based on the simulation results at the nanoscale.

In the GE/MoS₂ bilayer, the heat flux induced by a stable temperature gradient can be calculated as

$$J_B A_B = J_G A_G + J_M A_M . \quad (7.1)$$

The width of the GE/MoS₂ is denoted by w . The substitution of $A_B = t_B w$, $A_G = t_G w$, $A_M = t_M w$ and Fourier's law $J = -\lambda \nabla T$ into Eq. (7.1) arrives at

$$\lambda_B t_B \nabla T_B = \lambda_G t_G \nabla T_G + \lambda_M t_M \nabla T_M . \quad (7.2)$$

Figure 7.3(a) shows that the temperature distributions formed in the GE/MoS₂ bilayer, the constituent GE and MoS₂ layers overlap well and their temperature gradients ∇T only have minor difference, i.e., $\nabla T_B \approx \nabla T_G \approx \nabla T_M$. Note that this overlap still occurs when the length L of the bilayer increases. Thus, Eq. (7.2) can be approximated by the following simplified formula:

$$\lambda_B t_B = \lambda_G t_G \left(1 + \frac{\lambda_M t_M}{\lambda_G t_G}\right). \quad (7.3)$$

Simulation results show that the ratio of $\lambda_M t_M / \lambda_G t_G$ decreases as L increases, and the decrease becomes more dramatic especially when $L > 20$ nm. The ratio is about 0.1 at $L \approx 20$ nm and reduces to about 0.05 at $L \approx 100$ nm. Therefore, for a large length L , Eq. (7.3) can be approximately reduced to the following formula:

$$\lambda_B = \frac{t_G}{t_B} \lambda_G = 0.358 \lambda_G . \quad (7.4)$$

In Eq. (7.4), the λ_G of the GE layer in the bilayer can be approximated by that of an isolated GE monolayer because they are very close according to the previous discussion.

The increase of $\lambda_G t_G / \lambda_M t_M$ with the length L is because the GE and MoS₂ monolayers have different phonon MFPs, which leads to that they have different length dependences of thermal conductivity. The phonon MFP of the MoS₂ layer is ~ 18 nm [183], which is much smaller than that of the GE layer (~ 775 nm) [3]. When L is smaller than the phonon

MFP, the phonon transport is mainly ballistic and the thermal conductivity increases almost linearly with L . However, when L is larger than the phonon MFP, the phonon transport becomes diffusive and the increase in thermal conductivity slows down. Thus, when $20 < L < 775 \text{ nm}$, λ_G increases much faster than λ_M as L increases, thus leading to the decrease of $\lambda_M t_M / \lambda_G t_G$. Furthermore, when $L > 775 \text{ nm}$, the trend of the decrease of $\lambda_M t_M / \lambda_G t_G$ with L still remains until both λ_G and λ_M reach their respective saturated values.

Figure 7.5(a) compares the thermal conductivities of GE/MoS₂ bilayers at the nanoscale lengths predicted by Eq. (7.4) with the results obtained directly by MD simulation for the interaction strength scaling factor $\chi = 1$ and 5. It is found that the thermal conductivities λ_B obtained by both methods agree well for $\chi = 1$. As χ increases, the discrepancies between their results will increase. Nevertheless, such discrepancies fall within ~5% even though at $\chi = 5$, a value below which the scaling factor χ is generally tuned in practical application as discussed before.

To estimate the thermal conductivities of GE/MoS₂ bilayers at the microscale lengths, the extrapolation approach adopted in the previous studies [81, 151, 189, 194] is used. According to the kinetic theory of phonon transport, the reciprocal of thermal conductivity λ_G of the GE monolayer is a linear function of the reciprocal of its length L , i.e., $1/\lambda_G = A + B/L$. In Fig. 7.5(b), a linear fitting is conducted on the results obtained by MD simulations of the GE monolayers whose lengths range from 10 to 100 nm, which gives $A = 3.45 \times 10^{-4}$ and $B = 0.235$. Thus, λ_G of an infinitely long GE monolayer

($L \rightarrow \infty$) is $1/A = 2898 \text{ W/mK}$, while its phonon MFP can be obtained through $B/A = 681 \text{ nm}$. The two results agree well with the previously reported values of 2500-5000 W/mK [49, 111, 195, 196] and 775 nm [197], respectively.

Fig. 7.5. (a) Comparison of thermal conductivities of the GE/MoS₂ bilayers of various lengths obtained by MD simulation with those predicted by Eq. (7.4); (b) linear fitting of the MD simulation results to extrapolate the thermal conductivity of a GE monolayer at the microscale length.

Since the above discussion gives the λ_G in Eq. (7.4) as $1/\lambda_G = 3.45 \times 10^{-4} + 0.235/L$, Eq. (7.4) can finally be written as $\lambda_B = 0.358(3.45 \times 10^{-4} + 0.235/L)^{-1}$ for calculating the thermal conductivity of the GE/MoS₂ bilayer. Apparently, the λ_B for an infinitely long GE/MoS₂ bilayer ($L \rightarrow \infty$) is calculated to be 1037 W/mK.

It is worth pointing out that the thermal conductivity λ_B of infinite long isolated GE monolayer may show certain discrepancies for different methods, such as MD simulations and experiments. Even within the MD simulation scope, different simulation parameters and approaches would also lead to some discrepancies. However, the main finding of this work is that due to the weak interface interaction between the GE and MoS₂ monolayers,

the thermal conductivity λ_b of the GE/MoS₂ bilayer can be well approximated by that of the monolayer GE.

7.4. Out-of-plane interfacial thermal conductance

Figure 7.6 shows the evolution of the temperature difference ΔT between GE and MoS₂ during the thermal relaxation at $T = 300$ K. An overall exponential decay of ΔT is observed, as predicted by Eq. (6.8). The exponential fitting gives the relaxation time $\tau = 92.59$ ps. Thus, the interfacial thermal conductance G of the GE/MoS₂ bilayer at 300 K can be calculated to be 5.81 MW/m²K, according to Eq. (6.9). This value is much smaller than that of 11.74 MW/m²K found for the SE/GE bilayer system. The smaller G for the GE/MoS₂ may be rooted in the lower in-plane thermal conductivity of MoS₂ than that of SE.

Fig. 7.6. Evolution of the temperature difference between MoS₂ and GE during the thermal relaxation. Exponential fitting is performed to obtain the relaxation time τ .

The dependence of G on the temperature and interface coupling strength has also been studied and shown in Fig. 7.7. Similar trends are found as for the SE/GE bilayers,

i.e., G increases monotonically with both T and χ . As T increases from 200 to 500 K, G for GE/MoS₂ bilayers increases by about two times.

Fig. 7.7. Dependence of the interfacial thermal conductance G on the temperature T for different values of χ .

It is interesting to notice that the dependence of interface thermal conductance G of the GE/MoS₂ bilayer on the scaling factors χ is opposite to that of its in-plane thermal conductivity λ_b . Moreover, the former dependence is much stronger than the latter one. For example, at 300 K, as χ increases from 1 to 1.5, G increases by ~30% while λ_b stays almost unchanged. This result indicates that properly enhancing the interface coupling strength of the GE/MoS₂ bilayer is efficient in improving its out-of-plane interface thermal transport while does not affect its in-plane thermal conductivity.

7.5. Summary

The thermal transport in a GE/MoS₂ bilayer heterostructure is studied using MD simulation. The in-plane thermal conductivity and out-of-plane interface thermal

conductance of the GE/MoS₂ bilayer are calculated. An approximation approach is adopted to predict the thermal conductivity of micro-sized bilayers, based on the simulation results for nano-sized bilayers. It is found that the thermal conductivity λ_B of the GE/MoS₂ bilayer with a length $L > 20$ nm can be well predicted by the thermal conductivity λ_G of an isolated GE monolayer of the same length through the relationship: $\lambda_B = 0.358\lambda_G$ with $\lambda_G = (3.45 \times 10^{-4} + 0.235/L)^{-1}$. The λ_B of an infinitely long GE/MoS₂ bilayer is obtained to be 1037 W/mK.

In contrast to the high in-plane thermal conductivity λ_B of the GE/MoS₂ bilayer, its out-of-plane interface thermal conductance G is calculated as 5.81 MW/m²K, which is much lower than those of several other GE-based interfaces. Increase of the interface coupling strength scaling factor χ can dramatically increase G but with not much compromise in λ_B , implying that a proper increase of χ is profitable for improving the heat dissipation in GE/MoS₂ bilayer. Moreover, increase of the temperature can also increase G due to enhanced phonon coupling between GE and MoS₂, which is advantageous for heat dissipation between them when they work at high temperatures.

Currently, most of the experimental studies on the GE/MoS₂ bilayer focus on its electronic properties and its applications in electronic logics, memory devices, and lithium batteries. So far, no experimental studies have been reported on the thermal properties of the GE/MoS₂ bilayer, especially its interface thermal conductance, though some works have been conducted on individual GE or MoS₂ monolayers. This may mainly due to the difficulties in experimentally creating and measuring the temperature difference between

the GE and MoS₂ monolayers. For validation of the results predicted in this study, further experimental works are needed.

Chapter 8. Conclusions and Recommendations

Based on the works conducted during this PhD study, main conclusions are drawn and future works are recommended in this chapter.

8.1. Conclusions

Non-equilibrium MD simulation has been conducted to study the thermal properties of 2D nanomaterials including the hydrogenated GE, SE, GE/SE monolayers, GE/SE bilayer and GE/MoS₂ bilayer. The effects of structural alterations induced by hydrogenation, isotopic doping, strain and interfaces have been investigated, and their underlying mechanisms have been illustrated. Efficient methods that are able to tune the thermal properties of the 2D nanomaterials have been proposed. Moreover, the thermal rectification effect has been observed in both GE-based nanocomposites, which is meaningful to the development of novel thermal management devices. Specifically, the main conclusions that can be drawn from these investigations are listed as follows.

- Hydrogenation is efficient in tuning the thermal conductivity of GE. A small hydrogenation coverage of 10% will cause a large reduction of about 45% in the thermal conductivity. This reduction can be explained by the combination of two mechanisms: hydrogenation-induced enhancement of the coupling effect between the in-plane and out-of-plane phonon modes in GE, and the intensive phonon scattering effect between the hydrogenated and unhydrogenated carbon atoms. Among all the hydrogenation patterns, the RGO pattern can lead to the largest thermal conductivity reduction that can reach 75% and occurs at the hydrogen coverage of ~80%.

Meanwhile, it has been found that hydrogenation interrupts the planar morphology of GE and can lead to periodic ripples or local bucklings depending on the hydrogenation patterns.

- The thermal conductivity of SE is ~ 25 W/m K, which is much lower than that of GE, though they have similar honeycomb lattice structures. The low thermal conductivity of SE makes it promising for novel thermoelectric applications. Isotopic doping has proven to be a valid approach for reducing the thermal conductivity of SE, especially when the dopants have large atomic masses and are arranged in a superlattice structure. A maximum reduction up to 20% has been obtained for random doping with the isotopic atoms Si^{30} at the doping percentage of 50%. For isotopic doping with the superlattice structure, there exists a critical length (2.76 nm) of the superlattice period at which the minimum thermal conductivity was obtained. A competing mechanism between the interface scattering and confinement effects of the phonon modes has been identified to be responsible for the dependence of the thermal conductivity on the superlattice periodic length.
- Interfaces play an important role in the overall thermal conduction of GE-based nanocomposites. In both the hybrid GE/SE monolayer and bilayer, the interface thermal conductance is low, which becomes the main barrier for thermal dissipation. For the hybrid monolayer, the low interface thermal conductance of $250 \text{ MW/m}^2\text{K}$ is caused by the strong interface phonon scattering due to the phonon spectra mismatch; while for the hybrid bilayer, the low conductance of $11.28 \text{ MW/m}^2\text{K}$ is mainly

because of the thermal transport at the interface that is significantly limited by the weak coupling of the out-of-plane phonon modes.

- Thermal transport behaviors at the interface of 2D nanomaterials can be modified through interface engineering approaches such as strain engineering, hydrogenation and roughening. By eliminating the interface mismatch strain in the GE/SE monolayer heterostructure, its interface thermal conductance dramatically increases by ~70%. In the GE/SE bilayer heterostructure, the interface thermal conductance significantly increases when GE is hydrogenated. Moreover, the increase is largely dependent on the hydrogenation pattern and coverage. When GE is hydrogenated with the GO pattern at the hydrogen coverage of 50%, the interface thermal conductance of GE/SE bilayer increases the most by ~400%. For the isotope-doped SE with superlattices, when the interfaces between adjacent superlattice periods are roughened, the thermal conductivity of SE is reduced by ~20% and its dependence on the superlattice periodic length transforms from nonmonotonic to monotonic when heavy isotopic dopants are adopted.
- Thermal rectification effect has been observed in both the hybrid GE/SE monolayer and bilayer. The rectification ratio has been found to be comparable to several existing GE-based thermal rectifying structures. For the GE/SE monolayer, the rectification ratio depends on the monolayer length and the rectification effect is caused by the phonon mismatch across the GE/SE interface which induces different phonon scattering rates for two opposite heat transport directions. For the hybrid

bilayer, the rectification effect results from the asymmetric atomic densities and specific heat capacities of GE and SE.

8.2. Recommendations

A diverse range of novel technology drivers, including improved thermal dissipaters or barriers, more efficient thermoelectric energy conversion, thermal management of nanodevices and nanoparticles for thermal medical therapies, are motivating the studies of thermal properties of nanomaterials. In spite of tremendous works that have been conducted over the past years, the understanding of thermal transport behaviors at the nanoscale is still not well developed with many aspects being unexplored. In terms of the studies of thermal properties of 2D nanomaterials, the following future works are recommended.

Firstly, the effects of different functional groups on the thermal transport properties of GE can be investigated. In addition to hydrogenation considered in this study, many other functional groups, ranging from simplex halogen elements such as Br and Cl to protein molecule chains, can also be adopted to functionalize GE. These functional groups will impose different mass disorders and lattice-mismatch loadings on GE and thus may result in new features in its thermal transport behaviors. The interaction between the H atoms of the hydrogenated GE is weak, while the interactions between chemical groups can be much stronger, and thus bring new thermal transport phenomena.

Secondly, it will be interesting to study the thermal transport behaviors of nanostructures obtained by integrating simple GE-based structures. A good example would be the integration of GE/SE monolayers and GE/SE bilayers. In this study, the

thermal rectification effect has been observed at the interfaces of both GE/SE monolayers and bilayers. Moreover, in the GE/SE monolayers, heat flux prefers to flow from SE to GE; while in the GE/SE bilayers, the heat flux prefers to flow in an opposite direction. Therefore, if the GE/SE monolayers and bilayers are integrated, the heat flux can be designed in a controlled manner. As a result, it is possible to enhance the thermal rectification effects at the interfaces of the GE/SE monolayers and bilayers. With the development of advanced experimental techniques, GE can now be tailored and manipulated, which would lead to new nanostructures with novel thermal transport properties. These GE-based nanostructures will provide the basic bricks for the construction of complex architectures with fascinating properties and applications.

Thirdly, multiple material-engineering approaches can be applied to achieve the thermal properties of nanomaterials beyond their current limits. The strain engineering, chemical functionalization, doping and defect engineering have been identified as promising approaches for tuning the properties of nanomaterials. However, in most of the previous studies, only one single approach has been utilized or analyzed. As it is evidenced in the field of materials science, composite materials generally have superior properties over their constitute components. Hence, future study should focus on the combination of various material engineering methods for achieving superior nanomaterial properties.

Lastly, experimental works can be carried out to verify the results obtained in this study. For individual GE and MoS₂ monolayers, the thermal conductivities obtained from the MD simulation have been compared with those experimental results and shown good agreement. However, for the SE single layers, the GE/SE hybrid structures and the

GE/MoS₂ hybrid structures, the experimental measurements of their thermal properties are still not available. Future experimental studies in this area would be of great value.

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