Thermal Transport in 2D Materials

Subjects: Engineering, Mechanical

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Two-dimensional materials are characterized by excellent structural, mechanical, and physical properties, making them suitable for basic science and engineering applications because of their superb properties. In nanomaterials, thermal transport has revealed many unique phenomena, which, when understood, will open up new possibilities for the development of new nanotechnologies in thermal management. New technologies have become increasingly dependent on thermal conductivity as an essential parameter. Many benefits can be derived from nanoelectronic devices using 2D materials and they may potentially extend electronics into new fields of application.

2D materials thermal conductivity simulations

1. Introduction

A temperature increase occurs when advanced materials are used in some electronic applications. Increased thermal conductivity allows heat to diffuse faster and prevents large overheating, which can result in premature degradation. The majority of these unique phenomena are due to nanomaterials' notable properties. In fabrication and application, chemical functionalization, strain, and structural interruptions can alter their atomic structures, affecting their properties. Research on the micro/nano components of two-dimensional material has recently focused on their electrical, mechanical, and optical properties. It should be noted that for any micro/nano component, whether it is an electronic component or an optoelectronic component, the heat dissipation problem determines the device's performance and stability. High-density components will generate a lot of heat during high-speed operation. If the heat cannot be eliminated in time, it will cause the components to be too high in local and performance degradation, or even burnout. How to conduct immense heat away so that the components work in a relatively low-temperature environment becomes a common issue in the modern semiconductor industry [1][2][3][4][5].

An electronic device can generate heat in many different ways, such as by Joule heating, solar flux, or exothermic reactions. High-power density electronics such as integrated circuits, supercapacitors, LEDs, and lasers are notorious for localized Joule heating. Nanoscale devices have a higher power density, but a reduced amount of heat can be extracted as their dimensions decrease. Nanostructured solar cells and concentrated solar cells share a similar challenge of reducing efficiency with increased temperatures. For a final example, batteries can experience exothermic reactions and Joule heating, which may cause unwanted chemical reactions and device failure. Materials that must minimize heat transfer are at the other extreme. To reduce heat transfer across each leg, thermoelectric devices require materials with a low thermal conductivity. It creates a design conflict when

thermoelectric materials must also be good electrical conductors. To prevent heat from reaching critical parts, thermal insulation is designed.

Advances in the electronics industry have fueled an enormous demand for pioneering thermal management strategies to enhance the performance and reliability of devices by controlling energy dissipation generated in the devices. In nanoelectronics, where heat dissipation is a vital factor in the performance of high-density nanoscale circuits, or in thermoelectric materials, where low thermal conductivity is desired, controlling heat diffusion by controlling the phononic properties of fundamental components is a major interest.

2. Two-Dimensional (2D) Materials

Understanding material systems is at the core of the technology. Each application requires specific material properties. For example, circuits are built with copper because of their electrical conductivity, skyscrapers are constructed with concrete because of their compressive strength, and car tires are constructed with vulcanized rubber, which is pliable and durable. Nanomaterials refer to materials with a dimension of at least one nanometer in size. Qualitative changes in physicochemical properties and reactivity are related to the number of atoms or molecules determining the material in this scale.

Monolayer graphene flakes were isolated from bulk graphite by mechanical exfoliation, launching the field of two-dimensional (2D) materials [6]. There have also been numerous discoveries of 2D materials since then, including transition metal dichalcogenides (TMDs, e.g., MoS_2), hexagonal boron nitride (h-BN), and black phosphorus (BP) (or phosphorene). There is a wide range of physical properties available within the 2D materials family, from conducting graphene to semiconducting MoS_2 to insulating h-BN. As an added advantage, 2D crystal structures exhibit superior mechanical properties, exhibiting a high in-plane stiffness and strength, as well as an extremely low flexural rigidity. Together, the 2D materials have a wide range of potential applications [7][8].

Van der Waals forces or weak covalent bonds that hold together material layers can be mechanically or chemically exfoliated down to an in-plane, covalently bonded single layer. A 2D materials history dates back to the 1960s. As early as 1980, graphene, a one-atom thick graphite layer, was isolated and studied extensively as a monolayer. Novoselov and Geim introduced 2D materials by studying graphene under electric and magnetic fields [9]. Because of the high quality of the crystals and their ease of obtaining them, many researchers have developed more complicated 2D electron gas materials for graphene. A number of graphene effects were determined as a result. It has also been shown that other layered materials are known to mechanically exfoliate. Over a thousand materials have been identified by 2020 [10]. As layers often significantly influence the electrical, optical, and thermal properties of materials, this large number of materials can enable a plethora of novel physics. For example, by changing the gap energy, MoS_2 transitions from an indirect to a direct bandgap as the monolayer limit is reached.

Material properties are often thought to be determined solely by their material composition. Electricity is conducted by metals because they contain metallic bonds between their atoms, allowing electrons to drift freely throughout the material. The strength of concrete comes from the cement that rigidly locks incompressible sand and gravel

together. Vulcanized rubber is made of flexible polymer chains that are firmly linked together, making it both pliable and durable. The size of a material, however, can influence its behavior. Materials with nanoscale dimensions (i.e., whose sizes can be expressed in nanometers) are particularly susceptible to this. The nanoscale can affect electrical conductivity, chemical reactivity, mechanical properties, and even how a material interacts with light.

3. Thermal Conductivity

A greater understanding of the thermal properties of 2D nanomaterials is required due to their rapid development. The main factors contributing to this demand are as follows. First, electronic devices are subjected to ever-increasing thermal loads due to continuous miniaturization and component density increases. Electronic device components are getting smaller and smaller every year, according to Moore's law. One of the crucial components of electronics is the field-effect transistor, which has now reached a channel length of 100 nm, and a 50 nm channel length is on the horizon. Thermal design has become an essential part of electronic device development at the nanoscale, as controlling heat is critical for reliability and performance.

Furthermore, at the nanoscale, electronic devices exhibit thermal transport characteristics that are dramatically different from those observed at the macroscale. The electrical−thermal design of the electronic device should also take these features into account. As the use and requirement of energy sources increases, practical and efficient solutions are required for energy generation, consumption, and recycling. Heat management can be improved by utilizing recently developed nanotechnologies and nanomaterials. In some cases, for efficient thermal dissipation, nanomaterials with high thermal conductivities are employed in nanoscale electronics. A low thermal conductivity is required to increase thermal conversion or preservation in other cases, such as in thermoelectric devices and thermal barrier coatings, nanomaterials, or nanoparticles.

Heat is carried primarily by phonons in the same way electricity is carried by electrons. A recent study demonstrated that phonons can carry and process information as well [11]. A variety of types of thermal logic devices have been developed theoretically and even experimentally, such as thermal rectifiers [12][13], thermal transistors [14], thermal logic gates [15], and thermal memory cells [16]. In a similar manner to electronic circuits, thermal circuits can be fabricated using these basic thermal components.

Two-dimensional nanomaterials have different thermal properties than bulk materials due to their atomic structures. For example, graphene as a 2D material has a thermal conductivity as high as ~2000 W/m·K [17], or even higher [18]. This is comparable to the highest thermal conductivity material found in nature, which is diamond. As a result, high-power electronics could potentially benefit from its use in thermal management. h-BN also has high mechanical strength and good thermal properties. High-quality bulk h-BN samples could reach a thermal conductivity of ~390 W/m·K, indicating its potential as a current generation dielectric material [19]. In a study by Joe et al., the thermal conductivity of an 11-layer sample was found to reach about ~360 W/m·K [20]. For silicene, different MD simulations calculated thermal conductivities ranging from 5 to 50 W/m·K [21][22]. TMDs show different thermal conductivity. As an illustration, it has been estimated that MoS_2 has a thermal conductivity of about 26 W/m·K, according to Wei et al. [23]. WS_2 CVD-grown monolayer and bilayer thermal conductivity was determined by

Peimyoo et al. For monolayer and bilayer WS_2, the measured values are 32 and 53 W/m·K, respectively [24]. Theoretically, the thermal conductivity of phosphorene indicates low thermal conductivity. For instance, Qin et al. studied the simulated thermal conductivity along zigzag (ZZ) and armchair (AC) directions and found it to be 15.33 and 4.59 W/m·K, respectively [25]. However, during the manufacturing of 2D nanomaterials, structural defects such as voids, grain boundaries, and dislocations could be formed.

3.1. General Considerations and Solution Techniques

A heat flux equation, according to Fourier's law, can be expressed as follows [26]:

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+\dot{q}=\rho c_p\frac{\partial T}{\partial t} \quad (1)$$

Here, $\dot{q}$ is the rate of energy generated per unit volume of the medium (W/m^3) and k is the thermal conductivity (W/m·K). In Cartesian coordinates, Equation (1) is the general form of heat diffusion. There are two primary objectives that are usually attached to any conduction analysis. Known as the heat equation, it provides the basic tool for analyzing heat conduction. T (x, y, z) can be calculated as a function of time from its solution. For the present problem, the first objective is to detect the distribution of temperature in the medium and in order to do so, it is necessary to determine T (x, y). Solving the heat equation in the appropriate form is the key to obtaining this objective. It is found that in two-dimensional steady-state conditions with no generation and constant thermal conductivity, this form can be calculated from Equation (1) as follows:

$$\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}=0 \quad (2)$$

Equation (2) can be solved analytically by an exact mathematical solution. However, despite the fact that there are several techniques that can be used to solve these equations, the solutions usually involve complicated mathematical functions and series, and only a limited number of simple geometries and boundary conditions can be used. As a result of the dependent variable T being a continuous function of the independent variables (x, y), the solutions are valuable. Therefore, this solution can be used to calculate the temperature at any point within the medium.

3.2. The Method of Separation of Variables

Two-dimensional conduction problems can be solved with the separation of variables method by applying the boundary conditions to a thin rectangular plate, a long rectangular rod, or any other shape that can be described by

boundary conditions. By solving the heat equation, the temperature T corresponding value, heat flux, and heat flow lines can be determined, but this method is limited, complicated, and time-consuming [26].

3.3. *The Conduction Shape Factor*

The process of finding an analytical solution to a two-dimensional or three-dimensional heat equation can be time-consuming and even impossible in some cases. This leads to the consideration of a different approach. For example, the heat diffusion equation can be quickly solved in many examples by employing existing solutions to it to solve two- or three-dimensional conduction problems. Shape factor *S* or steady-state dimensionless conduction heat rates q_{ss}^{*} are used to present these solutions [26].

3.4. Thermal Transport at the Nanoscale

In order to transfer energy from one region of space to another region of space, the transportation or conduction of thermal energy requires the use of carriers, such as particles or waves. Except for alloys with extremely low electrical conductivity, metals conduct thermal energy mainly through electrons [27]. From a microscopic perspective, in dielectrics and semiconductors, it can be seen that heat is primarily carried by phonons or quantized vibrations of atoms in the lattice that can function as a particle to represent the phonon wave packets, according to the quantum state during their production. A phonon, when viewed from the angle of energy, will behave as a particle and collide with other phonon particles, as well as impurities and boundaries around it.

Firstly, before starting the detailed analysis, it is crucial that the length scales be clarified in advance. The figure shows a structure with a size of *L* (in 2D materials, *L* can be considered as the material's thickness) and a wavelength of *λ* for phonon wave packets. It is noted that the phonon is considered to be a particle in the spherical regime (gray regime). Phonons collide with other phonons, impurities, and boundaries when they move within solids. A phonon mean free path *Λ* is a distance between two collisions, which is an incredibly significant concept in the field of thermal transport. At room temperature, the mean free path *Λ* typically ranges from nanometers to tens of micrometers. It can be much longer at low temperatures. Generally, transport properties are discussed primarily on length scales larger than phonon wavelengths *λ* and comparable to or smaller than mean free paths *Λ*. When size *L* exceeds the mean free path *Λ*, the size effect will not be taken into consideration, which echoes the bulk of classical Fourier's law. A smaller size *L* than the mean free path *Λ* will result in phonons scattering on the boundaries before further phonon-to-phonon scattering. Due to these extra scatterings on the boundary, heat transfer will then be constrained by the boundaries. A primary cause of the reduction in thermal conductivity of 2D materials can be attributed to this phenomenon. It is known as the classical size effect when this type of effect occurs. In cases where the size *L* is smaller than the wavelength *λ*, it will encounter a quantum size effect as a result. A 2D material with a thickness of *L* usually exceeds the wavelength of the phonons unless the temperature is very low [27].

Materials, even crystals, do not have infinite thermal conductivity because phonons are scattered with one another. As result of this scattering, it is known as phonon−phonon scattering. High temperatures lead to stronger scattering

and shorter mean free paths Λ. There is a great deal of complexity involved when it comes to phonon–phonon scattering, and it can also be very challenging to determine the phonon–phonon scattering time. As a result of the advancement of computation algorithms and the availability of more powerful computation capabilities, there have been noticeable advances in the calculation of the phonon–phonon scattering rate through the first principle.

4. Simulation Methods

4.1. *Atomistic Simulations of Thermal Transport*

The thermal transport properties of a material can be predicted using atomic simulations by understanding its atomic structure and interatomic interactions. A variety of atomistic simulation approaches have been developed to study nanomaterial thermal transport properties.

To study the thermal transport properties of 2D materials, various theoretical methods have been introduced, including molecular dynamics simulations (MD), Boltzmann transport equations (BTE), and atomistic Green's functions (AGF).

4.2. Simulation Approaches

A variety of simulation techniques are presented for the study of material thermal properties [28]. The Boltzmann transport equation and the non-equilibrium Green's function are examples of first-class approaches. In each of these methods, the thermal properties are predicted by solving the lattice dynamics equations based on understanding the fundamentals of phonon properties. Direct MD simulation is used in the second class for calculating thermal properties, such as the equilibrium Green−Kubo approach and the non-equilibrium MD method (also called the direct approach).

4.3. A Mento Carlo Simulation Method

Boltzmann's equation for the transport of phonons usually forms the basis of a theoretical analysis of phonon transport [29]. To solve this equation in a closed-form manner, many critical assumptions and simplifications must be made, which can cause huge deviations from experimental observations, especially for materials whose geometrical and lattice structure are relatively complicated and whose defects are multiple types. The MC approach was originally developed as a numerical solution to the Boltzmann equation in the context of electron transport [29]. The method has been widely applied since then to manage the transport problems of particles. In bulk materials [30], thin films [31][32], nanowires [33], and nanocomposites [34], the MC simulation has been successfully applied to determine thermal transport properties.

4.4. First Principles Method

Using the Boltzmann transport equation (BTE) in conjunction with the Schrödinger equation, first principles calculations can be performed on thermal transport. For the first principles calculation, no fitting parameters are

required, as opposed to the traditional method of extracting phonon scattering times. The following steps are involved in the first principles of the thermal transport-based method. As a first step, first principles simulation refers to solving the Schrödinger equation numerically. Numerical computation is performed to calculate the atomic potential force constant. Based on these force constants, the anharmonic lattice dynamics will be used to extract the phonon dispersion relation and scattering rate. Then, the Boltzmann transport equation (BTE) can be linearized and solved numerically as well. As a result of this process, both the dispersion relation and the phonon scattering rate (or the relaxation time) for each phonon mode are calculated. Lastly, in order to calculate thermal conductivity, the lattice thermal connectivity can be extracted.

4.5. Molecular Dynamics Simulations Method

There is also another widely accepted method for thermal transport in 2D materials known as Molecular Dynamics (MD), which relies on Newton's law of motion as its physical foundation. Starting with the atomic potential between atoms, the process begins. As a result, the force acting on each atom can be calculated, as well as its velocity at any given moment. In the modern era of supercomputers, it is possible to determine the location of every atom at any time. Then, based on statistical mechanics principles, it is possible to study the expected macroscale properties.

4.6. Equilibrium Green−Kubo Approach

According to the equilibrium Green−Kubo approach, thermal conductivity is calculated by monitoring the dissipation time of these fluctuations. The Green−Kubo approach calculates the thermal conductivity of an isotropic material as follows [35]:

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

where $\langle \vec{J}(0)\vec{J}(t)\rangle$ is the autocorrelation function for heat flux and the angular brackets demonstrate ensemble averages. Here, T is the temperature, k_B is the Boltzmann constant, and V is the system volume.

4.7. Atomistic Green's Functions

Since it is evident, phonons are wave-like particles. Wave effects on a discrete atomic lattice can be accurately modeled using Atomistic Green's Functions (AGF). Initially, this method was introduced to deal with quantum electron transport in nanostructures [36][37][38][39][40][41][42]. The approach can be applied to a variety of nanostructures by making a few careful substitutions [43][44][45][46]. It is particularly suitable for low-dimensional heterostructures such as Si/Ge [47], graphene/h-BN [48], MoS_2/metal [49] interfaces, and others [50].

5. Experimental Measurement

5.1. Suspended Thermal Bridge Method

For the first time, the suspended thermal bridge method was used in micro/nano-scale thermal conductivity measurements in 2001. Previously, traditional methods could only measure the overall thermal conductivity of a bundle of nanowires. The phonon scattering between nanowires (or nanotubes) makes it impossible to accurately determine the thermal conductivity of a single sample [51]. The suspended thermal bridge method is more useful for the study of low-dimensional thermoelectric materials [52][53]. A thermal bridge microdevice is made of two suspended silicon nitride membranes (SiN_X) that are patterned with thin metal lines (Pt resistors).

5.2. Electron Beam Self-Heating Method

In the above-mentioned suspended thermal bridge method, the thermal contact resistance between the sample and the suspended platform is one of the main faults of this process. Although there are already some methods to improve it, the effect of this defect cannot be eliminated from the experimental principle. Researchers at Li Baowen's lab developed the electron beam self-heating method based on the suspended thermal bridge method in 2010 [54][55]. This method omits the influence of the contact thermal resistance between the sample and the suspended platform on the experimental results in principle and measures the spatial distribution of the thermal resistance of the micro/nano-scale materials. A scanning electron microscope (SEM) is used to measure the electron beam self-heating method.

5.3. Raman Method

In 2008, the first experimental measurement of the thermal conductivity of two-dimensional material, single-layer graphene in the suspended plane was the Raman method [56]. In two-dimensional materials, the Raman method has become one of the most important experimental methods for measuring thermal conduction. Several two-dimensional materials have been measured successfully using this method, including boron nitride [57][58], black phosphorus [59], and molybdenum sulfide [60][61][62]. The Raman method can be used to measure the thermal conductivity of two-dimensional materials by taking into account the following two factors: (1) Raman lasers can be used as heat sources because 2D materials have an absorption effect on them; (2) The Raman spectrum absorption peak positions of two-dimensional materials and a certain linear relationship between temperature [59][62][63]; in this way, the surface temperature of the material can be determined by the Raman spectrum of the material. The thermal conductivity of a two-dimensional material can be calculated by combining the two principles mentioned above through the heat conduction model.

5.4. Time-Domain Thermoreflectance Method

In 1983, Eesley applied the picosecond pulsed laser to detect the non-equilibrium heat transport process in metallic copper [64] since the time-domain thermoreflectance (TDTR) method has been formally applied to the measurement of material thermal properties. The TDTR method has been developed over a period of thirty years.

It has now become one of the most widely used methods for measuring the thermal properties of materials in an unsteady state. This method is usually employed to measure the thermal conductivity and interfacial thermal resistance of materials [65][66][67]. Its basic principle is that a beam of a femtosecond pulsed laser is divided into a pump light and a probe light through a beam splitter. In this system, the pump light is used as a heat source for heating the surface of the material, and the probe light measures the change in the surface temperature of the material (the reflectivity of the material surface to the laser is related to the temperature). The displacement platform can accurately control the optical path difference between the two beams and then control the time interval between them to reach the surface of the material, resulting in a certain time delay (t_d).

5.5. Micro-Suspended-Pad Method

The suspended-pad method, first used to measure carbon nanotubes [68] and silicon nanowires [69][70], is another method frequently used for nanostructures, nanoribbons, and 2D materials. The micro-pad devices are manufactured in batches as part of this method. A device consists of two adjacent silicon nitride membranes suspended by a silicon nitride long beam [70]. The patterned platinum heaters are manufactured on both the pads and long beams. Normally, samples are transferred using a nanomanipulator. Utilizing focused ion-beam deposition, the thermal contacts can be increased by Pt deposition, making the contacts electrically and thermally ohmic. It is, therefore, possible to ignore the thermal resistance of the junction. Various 2D materials have been measured using the suspended-pad method, such as h-BN [20], black phosphorus [71], and MoS_2 [72]. Due to the accuracy of this method, the electrical signal can be very precisely derived.

6. 2D Thermal Conductivity

6.1. Graphene

As the first 2D material successfully prepared, graphene became the favorite of scientific research once discovered. It has a series of excellent physical properties including ultra-high conductivity, ultra-high carrier mobility, etc. [9][73][74]. In terms of thermal conductivity, graphene also performs well, and its intrinsic thermal conductivity at room temperature can reach 2000–3000 W/m·K, which is the highest thermal conductivity material found so far. In 2008, for the first time, Balandin et al. [75] measured the thermal conductivity of suspended single-layer graphene at room temperature using the Raman method and graphite bulk materials reaching 4840–5300 W/m·K; however, upon further study by scientists, it was discovered that the experiment may have had an excessive estimate of the Raman laser absorption power of graphene, resulting in a result 4–6 times larger [18][76].

The results illustrate that the thermal conductivity of single-layer graphene grown by chemical vapor deposition (CVD) is around 2500–3100 W/m·K (T = 350 K) and 1200–1400 W/m·K (T = 500 K). It has also been found that the shape, size, and measurement environment of the suspended part of the graphene will affect the final result. In addition to the dispute about the laser absorption rate, it caused the difference between different experimental results. Another major reason for the large difference is that the preparation methods of graphene are different

(mechanical exfoliation or chemical vapor deposition), resulting in certain differences in its quality (impurities, grain boundaries, organic residues, etc.). These factors will affect the phonon and generate additional scattering.

6.2. Boron Nitride

Due to the large bandgap and the very smooth surface, boron nitride (h-BN) is an ideal type of dielectric material. At the same time, the thermal conductivity of boron nitride bulk materials (about 400 W/m·K, room temperature) is very close to copper, and its mass is much lower than copper under the same volume, so it has broad application prospects in terms of the heat dissipation of electronic devices [77][78]. Boron nitride is called white graphene. The crystal structure is similar to graphene. Nitrogen atoms and boron atoms in the plane are interlaced to form a honeycomb structure, and the layers are combined with each other by van der Waals forces. It is one of the two-dimensional materials discovered earlier [79].

6.3. Molybdenum Sulfide and Other Transition Metal Sulfides

Transition metal sulfides (MX_2, where M is transition metal elements such as Mo, W, Ti, and X represents chalcogen elements, including S, Se, and Te) are a very important group of two-dimensional materials and their crystal structure is a “sandwich”-like layered structure [80]. Unlike single-layer graphene, single-layer boron nitride, and other two-dimensional materials that only contain one atomic layer, a single-layer transition metal sulfide contains three atomic layers (the transition metal atomic layer is sulfurized).

Molybdenum sulfide is the most widely studied transition metal sulfide. Because of its controllable bandgap and excellent electrical properties, it can also exist stably in the air. It is considered a material for the next generation of microelectronic devices with great potential. Optics, thermoelectrics, and other fields also have certain application prospects [81][82][83].

6.4. Black Phosphorus, Black Arsenic

Due to the advantages of the controllable bandgap and relatively high switching, black phosphorous (BP) is one of the first materials for the next generation of microelectronic devices to be studied [84][85][86]. However, initially, researchers were interested in the thermal conductivity of black phosphorous. This is mainly because of its in-plane anisotropic “Great Wall”-like structure [71], which may lead to the anisotropy of thermal conductivity [87]. It is worth noting that the black phosphorous pole is easy to oxidize, so in experiments with black phosphorus, the exposure time of the sample in the air needs to be strictly controlled. Qin et al. [88] predicted the room temperature surface of the single-layer black phosphorus along the Zigzag (ZZ) direction and the (Armchair) AC direction through theoretical research. The internal thermal conductivity ratio can reach 30.15 W/m·K in the ZZ direction and 13.65 W/m·K in the AC direction, and due to its “Great Wall”-like structure, the out-of-plane phonon mode has a positive effect on the thermal conductivity. The contribution of efficiency is very low (about 5%). Lou et al. [59] experimentally measured the in-plane thermal conductivity of the multi-layer black phosphorus with different thicknesses at room temperature and the smallest thickness was ~10 nm. The thermal conductivity in the ZZ direction is 20 W/m·K, while the thermal conductivity in the AC direction is only ~10 W/m·K, which confirms the above theoretical

prediction. As the same main group element of phosphorus, arsenic, i.e., black arsenic (Bas), has a crystal structure similar to black phosphorus and also has a significant in-plane thermal conductivity anisotropy effect.

6.5. Telluride

Bulk tellurium (Te) is a new and high-quality thermoelectric material [89]. At the same time, due to its two-dimensional structure, telluride can be used as an effective means to further improve its thermoelectric properties [90]. In the bulk material, the tellurium atom is combined with a neighboring atom through a covalent bond and extends in a spiral shape. Adjacent spiral chains are then combined by van der Waals forces [91], so bulk tellurium belongs to a quasi-one-dimensional chain structure. However, the theory predicts that the structure of monolayer telluride is different from that of bulk tellurium. There are three possible crystal structures (α-Te, β-Te, γ-Te) [92].

References

1. Kobayashi, M. More than Moore. Kyokai Joho Imeji Zasshi/J. Inst. Image Inf. Telev. Eng. 2016, 70, 324–327.
2. Russ, B.; Glaudell, A.; Urban, J.J.; Chabinyc, M.L.; Segalman, R.A. Organic Thermoelectric Materials for Energy Harvesting and Temperature Control. Nat. Rev. Mater. 2016, 1, 16050.
3. Saraiva, E.F.; Milan, L.A. Clustering Gene Expression Data Using a Posterior Split-Merge-Birth Procedure. Scand. J. Stat. 2012, 39, 399–415.
4. Xu, X.; Zhou, J.; Chen, J. Thermal Transport in Conductive Polymer–Based Materials. Adv. Funct. Mater. 2020, 30, 1904704.
5. Moore, A.L.; Shi, L. Emerging Challenges and Materials for Thermal Management of Electronics. Mater. Today 2014, 17, 163–174.
6. Novoselov, K.S.; Jiang, D.; Schedin, F.; Booth, T.J.; Khotkevich, V.V.; Morozov, S.V.; Geim, A.K. Two-Dimensional Atomic Crystals. Proc. Natl. Acad. Sci. USA 2005, 102, 10451–10453.
7. Butler, S.Z.; Hollen, S.M.; Cao, L.; Cui, Y.; Gupta, J.A.; Gutiérrez, H.R.; Heinz, T.F.; Hong, S.S.; Huang, J.; Ismach, A.F.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. ACS Nano 2013, 7, 2898–2926.
8. Bhimanapati, G.R.; Lin, Z.; Meunier, V.; Jung, Y.; Cha, J.; Das, S.; Xiao, D.; Son, Y.; Strano, M.S.; Cooper, V.R.; et al. Recent Advances in Two-Dimensional Materials beyond Graphene. ACS Nano 2015, 9, 11509–11539.
9. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric Field Effect in Atomically Thin Carbon Films. Science 2004, 306, 666–669.

10. Mounet, N.; Gibertini, M.; Schwaller, P.; Campi, D.; Merkys, A.; Marrazzo, A.; Sohier, T.; Castelli, I.E.; Cepellotti, A.; Pizzi, G.; et al. Two-Dimensional Materials from High-Throughput Computational Exfoliation of Experimentally Known Compounds. Nat. Nanotechnol. 2018, 13, 246–252.
11. Wang, L.; Li, B. Phononics Gets Hot. Phys. World 2008, 21, 27–29.
12. Hu, B.; Yang, L.; Zhang, Y. Asymmetric Heat Conduction in Nonlinear Lattices. Phys. Rev. Lett. 2006, 97, 2–5.
13. Xie, Z.X.; Li, K.M.; Tang, L.M.; Pan, C.N.; Chen, K.Q. Nonlinear Phonon Transport and Ballistic Thermal Rectification in Asymmetric Graphene-Based Three Terminal Junctions. Appl. Phys. Lett. 2012, 100, 183110.
14. Lo, W.C.; Wang, L.; Li, B. Thermal Transistor: Heat Flux Switching and Modulating. J. Phys. Soc. Jpn. 2008, 77, 54402.
15. Wang, L.; Li, B. Thermal Logic Gates: Computation with Phonons. Phys. Rev. Lett. 2007, 99, 177208.
16. Wang, L.; Li, B. Thermal Memory: A Storage of Phononic Information. Phys. Rev. Lett. 2008, 101, 267203.
17. Madelung, O.; Klemens, P.G.; Neuer, G.; White, G.K.; Sundqvist, B.; Uher, C. Thermal Conductivity of Pure Metals and Alloys/Wärmeleitfähigkeit von Reinen Metallen Und Legierungen; Springer: Berlin/Heidelberg, Germany, 1991; Volume 3.
18. Balandin, A.A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C.N. Superior Thermal Conductivity of Single-Layer Graphene. Nano Lett. 2008, 8, 902–907.
19. Geick, R.; Perry, C.H.; Rupprecht, G. Normal Modes in Hexagonal Boron Nitride. Phys. Rev. 1966, 146, 543–547.
20. Jo, I.; Pettes, M.T.; Kim, J.; Watanabe, K.; Taniguchi, T.; Yao, Z.; Shi, L. Thermal Conductivity and Phonon Transport in Suspended Few-Layer Hexagonal Boron Nitride. Nano Lett. 2013, 13, 550–554.
21. Liu, B.; Reddy, C.D.; Jiang, J.; Zhu, H.; Baimova, J.A.; Dmitriev, S.V.; Zhou, K. Thermal Conductivity of Silicene Nanosheets and the Effect of Isotopic Doping. J. Phys. D Appl. Phys. 2014, 47, 165301.
22. Zhang, X.; Xie, H.; Hu, M.; Bao, H.; Yue, S.; Qin, G.; Su, G. Thermal Conductivity of Silicene Calculated Using an Optimized Stillinger-Weber Potential. Phys. Rev. B Condens. Matter Mater. Phys. 2014, 89, 054310.
23. Wei, X.; Wang, Y.; Shen, Y.; Xie, G.; Xiao, H.; Zhong, J.; Zhang, G. Phonon Thermal Conductivity of Monolayer MoS2: A Comparison with Single Layer Graphene. Appl. Phys. Lett. 2014, 105, 2–7.

24. Peimyoo, N.; Shang, J.; Yang, W.; Wang, Y.; Cong, C.; Yu, T. Thermal Conductivity Determination of Suspended Mono- and Bilayer WS2 by Raman Spectroscopy. Nano Res. 2015, 8, 1210–1221.
25. Qin, G.; Zhang, X.; Yue, S.-Y.; Qin, Z.; Wang, H.; Han, Y.; Hu, M. Resonant Bonding Driven Giant Phonon Anharmonicity and Low Thermal Conductivity of Phosphorene. Phys. Rev. B 2016, 94, 165445.
26. Bergman, T.L.; Incropera, F.P.; DeWitt, D.P.; Lavine, A.S. Fundamentals of Heat and Mass Transfer; John Wiley & Sons: New York, NY, USA, 2011; ISBN 0470501979.
27. Chen, X.K.; Zeng, Y.J.; Chen, K.Q. Thermal Transport in Two-Dimensional Heterostructures. Front. Mater. 2020, 7, 578791.
28. Goddard, W.A., III; Brenner, D.; Lyshevski, S.E.; Iafrate, G.J. Handbook of Nanoscience, Engineering, and Technology, 1st ed.; CRC Press: Boca Raton, FL, USA, 2002.
29. Chen, Y.; Li, D.; Lukes, J.R.; Majumdar, A. Monte Carlo Simulation of Silicon Nanowire Thermal Conductivity. J. Heat Transf. 2005, 127, 1129–1137.
30. Lacroix, D.; Joulain, K.; Lemonnier, D. Monte Carlo Transient Phonon Transport in Silicon and Germanium at Nanoscales. Phys. Rev. B Condens. Matter Mater. Phys. 2005, 72, 064305.
31. Mazumder, S.; Majumdar, A. Monte Carlo Study of Phonon Transport in Solid Thin Films Including Dispersion and Polarization. J. Heat Transf. 2001, 123, 749–759.
32. Aksamija, Z.; Knezevic, I. Anisotropy and Boundary Scattering in the Lattice Thermal Conductivity of Silicon Nanomembranes. Phys. Rev. B Condens. Matter Mater. Phys. 2010, 82, 045319.
33. Ramayya, E.B.; Maurer, L.N.; Davoody, A.H.; Knezevic, I. Thermoelectric Properties of Ultrathin Silicon Nanowires. Phys. Rev. B Condens. Matter Mater. Phys. 2012, 86, 115328.
34. Jeng, M.-S.; Yang, R.; Song, D.; Chen, G. Modeling the Thermal Conductivity and Phonon Transport in Nanoparticle Composites Using Monte Carlo Simulation. J. Heat Transf. 2008, 130, 042410.
35. Schelling, P.K.; Phillpot, S.R.; Keblinski, P. Comparison of Atomic-Level Simulation Methods for Computing Thermal Conductivity. Phys. Rev. B Condens. Matter Mater. Phys. 2002, 65, 144306.
36. Deng, Y.X.; Chen, S.Z.; Zeng, Y.; Feng, Y.; Zhou, W.X.; Tang, L.M.; Chen, K.Q. Spin Gapless Semiconductor and Half-Metal Properties in Magnetic Penta-Hexa-Graphene Nanotubes. Org. Electron. 2018, 63, 310–317.
37. Zeng, J.; Chen, K.Q.; Tong, Y.X. Covalent Coupling of Porphines to Graphene Edges: Quantum Transport Properties and Their Applications in Electronics. Carbon 2018, 127, 611–617.
38. Chen, T.; Xu, L.; Li, Q.; Li, X.; Long, M. Direction and Strain Controlled Anisotropic Transport Behaviors of 2D GeSe-Phosphorene VdW Heterojunctions. Nanotechnology 2019, 30, 445703.

39. Zhou, Y.; Zheng, X.; Cheng, Z.Q.; Chen, K.Q. Current Superposition Law Realized in Molecular Devices Connected in Parallel. J. Phys. Chem. C 2019, 123, 10462–10468.
40. Fan, Z.Q.; Zhang, Z.H.; Yang, S.Y. High-Performance 5.1 Nm in-Plane Janus WSeTe Schottky Barrier Field Effect Transistors. Nanoscale 2020, 12, 21750–21756.
41. Fan, Z.Q.; Chen, K.Q. Negative Differential Resistance and Rectifying Behaviors in Phenalenyl Molecular Device with Different Contact Geometries. Appl. Phys. Lett. 2010, 96, 23–26.
42. Chen, T.; Guo, C.; Xu, L.; Li, Q.; Luo, K.; Liu, D.; Wang, L.; Long, M. Modulating the Properties of Multi-Functional Molecular Devices Consisting of Zigzag Gallium Nitride Nanoribbons by Different Magnetic Orderings: A First-Principles Study. Phys. Chem. Chem. Phys. 2018, 20, 5726–5733.
43. Xu, Y.; Chen, X.; Gu, B.L.; Duan, W. Intrinsic Anisotropy of Thermal Conductance in Graphene Nanoribbons. Appl. Phys. Lett. 2009, 95, 10–13.
44. He, J.; Li, D.; Ying, Y.; Feng, C.; He, J.; Zhong, C.; Zhou, H.; Zhou, P.; Zhang, G. Orbitally Driven Giant Thermal Conductance Associated with Abnormal Strain Dependence in Hydrogenated Graphene-like Borophene. NPJ Comput. Mater. 2019, 5, 47.
45. Zhou, Y.H.; Zhang, X.; Ji, C.; Liu, Z.M.; Chen, K.Q. The Length and Hydrogenation Effects on Electronic Transport Properties of Carbon-Based Molecular Wires. Org. Electron. 2017, 51, 332–340.
46. Peng, X.F.; Chen, K.Q. Thermal Transport for Flexural and In-Plane Phonons in Graphene Nanoribbons. Carbon 2014, 77, 360–365.
47. Tian, Z.; Esfarjani, K.; Chen, G. Enhancing Phonon Transmission across a Si/Ge Interface by Atomic Roughness: First-Principles Study with the Green's Function Method. Phys. Rev. B Condens. Matter Mater. Phys. 2012, 86, 235304.
48. Peng, X.F.; Zhou, X.; Tan, S.H.; Wang, X.J.; Chen, L.Q.; Chen, K.Q. Thermal Conductance in Graphene Nanoribbons Modulated by Defects and Alternating Boron-Nitride Structures. Carbon 2017, 113, 334–339.
49. Yan, Z.; Chen, L.; Yoon, M.; Kumar, S. The Role of Interfacial Electronic Properties on Phonon Transport in Two-Dimensional MoS2 on Metal Substrates. ACS Appl. Mater. Interfaces 2016, 8, 33299–33306.
50. Ma, D.; Ding, H.; Meng, H.; Feng, L.; Wu, Y.; Shiomi, J.; Yang, N. Nano-Cross-Junction Effect on Phonon Transport in Silicon Nanowire Cages. Phys. Rev. B 2016, 94, 165434.
51. Hone, J.; Whitney, M.; Piskoti, C.; Zettl, A. Thermal Conductivity of Single-Walled Carbon Nanotubes. Phys. Rev. B 1999, 59, R2514–R2516.
52. Hochbaum, A.I.; Chen, R.; Delgado, R.D.; Liang, W.; Garnett, E.C.; Najarian, M.; Majumdar, A.; Yang, P. Enhanced Thermoelectric Performance of Rough Silicon Nanowires. Nature 2008, 451,

163–167.

53. Guo, J.; Huang, Y.; Wu, X.; Wang, Q.; Zhou, X.; Xu, X.; Li, B. Thickness-Dependent In-Plane Thermal Conductivity and Enhanced Thermoelectric Performance in p-Type ZrTe5 Nanoribbons. Phys. Status Solidi RRL 2019, 13, 1800529.
54. Wang, Z.; Xie, R.; Bui, C.T.; Liu, D.; Ni, X.; Li, B.; Thong, J.T.L. Thermal Transport in Suspended and Supported Few-Layer Graphene. Nano Lett. 2011, 11, 113–118.
55. Aiyiti, A.; Bai, X.; Wu, J.; Xu, X.; Li, B. Measuring the Thermal Conductivity and Interfacial Thermal Resistance of Suspended MoS2 Using Electron Beam Self-Heating Technique. Sci. Bull. 2018, 63, 452–458.
56. Shi, L.; Li, D.; Yu, C.; Jang, W.; Kim, D.; Yao, Z.; Kim, P.; Majumdar, A. Measuring Thermal and Thermoelectric Properties of One-Dimensional Nanostructures Using a Microfabricated Device. J. Heat Transf. 2003, 125, 881–888.
57. Lin, Z.; Liu, C.; Chai, Y. High Thermally Conductive and Electrically Insulating 2D Boron Nitride Nanosheet for Efficient Heat Dissipation of High-Power Transistors. 2D Mater. 2016, 3, 041009.
58. Cai, Q.; Scullion, D.; Gan, W.; Falin, A.; Zhang, S.; Watanabe, K.; Taniguchi, T.; Chen, Y.; Santos, E.J.G.; Li, L.H. High Thermal Conductivity of High-Quality Monolayer Boron Nitride and Its Thermal Expansion. Sci. Adv. 2022, 5, eaav0129.
59. Luo, Z.; Maassen, J.; Deng, Y.; Du, Y.; Garrelts, R.P.; Lundstrom, M.S.; Ye, P.D.; Xu, X. Anisotropic In-Plane Thermal Conductivity Observed in Few-Layer Black Phosphorus. Nat. Commun. 2015, 6, 8572.
60. Yan, R.; Simpson, J.R.; Bertolazzi, S.; Brivio, J.; Watson, M.; Wu, X.; Kis, A.; Luo, T.; Hight Walker, A.R.; Xing, H.G. Thermal Conductivity of Monolayer Molybdenum Disulfide Obtained from Temperature-Dependent Raman Spectroscopy. ACS Nano 2014, 8, 986–993.
61. Yu, Y.; Minhaj, T.; Huang, L.; Yu, Y.; Cao, L. In-Plane and Interfacial Thermal Conduction of Two-Dimensional Transition-Metal Dichalcogenides. Phys. Rev. Appl. 2020, 13, 034059.
62. Sahoo, S.; Gaur, A.P.S.; Ahmadi, M.; Guinel, M.J.F.; Katiyar, R.S. Temperature-Dependent Raman Studies and Thermal Conductivity of Few-Layer MoS2. J. Phys. Chem. C 2013, 117, 9042–9047.
63. Zhou, H.; Zhu, J.; Liu, Z.; Yan, Z.; Fan, X.; Lin, J.; Wang, G.; Yan, Q.; Yu, T.; Ajayan, P.M.; et al. High Thermal Conductivity of Suspended Few-Layer Hexagonal Boron Nitride Sheets. Nano Res. 2014, 7, 1232–1240.
64. Tripp, R.; Ferro-Luzzi, M.; Glashow, S.; Rosenfeld, A. Physical Review Letters. Nature 1958, 182, 227–228.
65. Sood, A.; Xiong, F.; Chen, S.; Cheaito, R.; Lian, F.; Asheghi, M.; Cui, Y.; Donadio, D.; Goodson, K.E.; Pop, E. Quasi-Ballistic Thermal Transport Across MoS2 Thin Films. Nano Lett. 2019, 19,

2434–2442.

66. Jiang, P.; Qian, X.; Gu, X.; Yang, R. Probing Anisotropic Thermal Conductivity of Transition Metal Dichalcogenides MX2 (M = Mo, W and X = S, Se) Using Time-Domain Thermoreflectance. Adv. Mater. 2017, 29, 1701068.
67. Islam, A.; Van Den Akker, A.; Feng, P.X.L. Anisotropic Thermal Conductivity of Suspended Black Phosphorus Probed by Opto-Thermomechanical Resonance Spectromicroscopy. Nano Lett. 2018, 18, 7683–7691.
68. Kim, P.; Shi, L.; Majumdar, A.; McEuen, P.L. Thermal Transport Measurements of Individual Multiwalled Nanotubes. Phys. Rev. Lett. 2001, 87, 215502.
69. Cahill, D.G. Thermal-Conductivity Measurement by Time-Domain Thermoreflectance. MRS Bull. 2018, 43, 768–774.
70. Li, D.; Wu, Y.; Kim, P.; Shi, L.; Yang, P.; Majumdar, A. Thermal Conductivity of Individual Silicon Nanowires. Appl. Phys. Lett. 2003, 83, 2934–2936.
71. Lee, S.; Yang, F.; Suh, J.; Yang, S.; Lee, Y.; Li, G.; Choe, H.S.; Suslu, A.; Chen, Y.; Ko, C.; et al. Anisotropic In-Plane Thermal Conductivity of Black Phosphorus Nanoribbons at Temperatures Higher than 100 K. Nat. Commun. 2015, 6, 8573.
72. Jo, I.; Pettes, M.T.; Ou, E.; Wu, W.; Shi, L. Basal-Plane Thermal Conductivity of Few-Layer Molybdenum Disulfide. Appl. Phys. Lett. 2014, 104, 201902.
73. Zhang, Y.; Tan, Y.W.; Stormer, H.L.; Kim, P. Experimental Observation of the Quantum Hall Effect and Berry's Phase in Graphene. Nature 2005, 438, 201–204.
74. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Katsnelson, M.I.; Grigorieva, I.V.; Dubonos, S.V.; Firsov, A.A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. Nature 2005, 438, 197–200.
75. Carslaw, H.S.; Jaeger, J.C. Conduction of Heat in Solids; Oxford University Press: London, UK, 1959.
76. Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E.P.; Nika, D.L.; Balandin, A.A.; Bao, W.; Miao, F.; Lau, C.N. Extremely High Thermal Conductivity of Graphene: Prospects for Thermal Management Applications in Nanoelectronic Circuits. Appl. Phys. Lett. 2008, 92, 151911.
77. Duclaux, L.; Nysten, B.; Issi, J.-P.; Moore, A.W. Structure and Low-Temperature Thermal Conductivity of Pyrolytic Boron Nitride. Phys. Rev. B 1992, 46, 3362–3367.
78. Simpson, A.; Stuckes, A.D. The Thermal Conductivity of Highly Oriented Pyrolytic Boron Nitride. J. Phys. C Solid State Phys. 1971, 4, 1710–1718.

79. Alem, N.; Erni, R.; Kisielowski, C.; Rossell, M.D.; Gannett, W.; Zettl, A. Atomically Thin Hexagonal Boron Nitride Probed by Ultrahigh-Resolution Transmission Electron Microscopy. Phys. Rev. B 2009, 80, 155425.
80. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically Thin MoS2: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 2010, 105, 2–5.
81. Liu, X.; Zhang, G.; Pei, Q.X.; Zhang, Y.W. Phonon Thermal Conductivity of Monolayer MoS2 Sheet and Nanoribbons. Appl. Phys. Lett. 2013, 103, 133113.
82. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS2 Transistors. Nat. Nanotechnol. 2011, 6, 147–150.
83. Liu, X.; Zhang, Y.W. Thermal Properties of Transition-Metal Dichalcogenide. Chin. Phys. B 2018, 27, 034402.
84. Villegas, C.E.P.; Rocha, A.R.; Marini, A. Anomalous Temperature Dependence of the Band Gap in Black Phosphorus. Nano Lett. 2016, 16, 5095–5101.
85. Zhang, Y.; Zheng, Y.; Rui, K.; Hng, H.H.; Hippalgaonkar, K.; Xu, J.; Sun, W.; Zhu, J.; Yan, Q.; Huang, W. 2D Black Phosphorus for Energy Storage and Thermoelectric Applications. Small 2017, 13, 1700661.
86. Li, L.; Yu, Y.; Ye, G.J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X.H.; Zhang, Y. Black Phosphorus Field-Effect Transistors. Nat. Nanotechnol. 2014, 9, 372–377.
87. Hong, Y.; Zhang, J.; Cheng Zeng, X. Thermal Transport in Phosphorene and Phosphorene-Based Materials: A Review on Numerical Studies. Chin. Phys. B 2018, 27, 36501.
88. Qin, G.; Yan, Q.-B.; Qin, Z.; Yue, S.-Y.; Hu, M.; Su, G. Anisotropic Intrinsic Lattice Thermal Conductivity of Phosphorene from First Principles. Phys. Chem. Chem. Phys. 2015, 17, 4854–4858.
89. Lin, S.; Li, W.; Chen, Z.; Shen, J.; Ge, B.; Pei, Y. Tellurium as a High-Performance Elemental Thermoelectric. Nat. Commun. 2016, 7, 10287.
90. Reed, E.J. Two-Dimensional Tellurium. Nature 2017, 552, 40–41.
91. Du, Y.; Qiu, G.; Wang, Y.; Si, M.; Xu, X.; Wu, W.; Ye, P.D. One-Dimensional van Der Waals Material Tellurium: Raman Spectroscopy under Strain and Magneto-Transport. Nano Lett. 2017, 17, 3965–3973.
92. Qiao, J.; Pan, Y.; Yang, F.; Wang, C.; Chai, Y.; Ji, W. Few-Layer Tellurium: One-Dimensional-like Layered Elementary Semiconductor with Striking Physical Properties. Sci. Bull. 2018, 63, 159–168.