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• REVIEW •
Special Focus on Two-Dimensional Materials and Device Applications

Filling the gap: thermal properties and device applications of graphene

Rui WU[1], Rui-Zhi ZHU[1], Shi-Hui ZHAO[1], Gang ZHANG[2*], He TIAN[1*] & Tian-Ling REN[1*]

[1]*Institute of Microelectronics and Beijing National Research Center for Information Science and Technology (BNRist), Tsinghua University, Beijing* 100084*, China;*
[2]*Institute of High Performance Computing, A*STAR, Singapore* 138632*, Singapore*

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Abstract With the miniaturization and integration of electronic devices, the heat dissipation problems caused by higher power density are getting more serious, limiting the development of integrated circuits industry. Graphene, as a representative of two-dimensional materials, has attracted extensive attention for its excellent thermal properties. Ever since it has been discovered, researches have been carried out and achievements have been made both theoretically and practically. Here, we review the established theories and simulation system for 2D heat conduction, different measurement methods for thermal conductivity and graphene's device applications. We propose two gaps between different scales and between theoretical prediction and practical effect. Owing to the higher heat dissipation requirements and the endless pursuit of better thermal performance, it is challenging but critical to continue studying and further understand the thermal properties of graphene. Challenges and opportunities are both emphasized. It is hoped that the diversification and progress in morphology and manufacturing technology can bring new development and that graphene can eventually be widely used and make huge changes to micoelectronic industry.

Keywords graphene, thermal properties, device application, thermal conductivity, 2D material

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1 Introduction

With the fast development of microelectronic industry, the integration level of electronic devices is reaching a grand new level, leading to higher power density and more heat production. Thus, the hotspot and heat dissipation problems are increasingly more serious, which observably reduce the lifespan of devices and cause lots of other problems such as bad customer experience. Therefore, better heat dissipation efficiency is crucial for the breakthrough of existing bottlenecks. Since the limitation of development, lots of efforts have been made to improve and solve the problem. People have turned to graphene, the two dimensional material obtained by mechanical exfoliation in 2004 by Novoselov et al. [1], for its ultra-high thermal conductivity (TC) and excellent thermal properties. Many researches on experimental measurement and simulation of graphene's TC have been carried out and researchers are keen on studies about graphene layer's applications as well. However, despite the promising results from experiments and simulations indicating a bright prospect in efficient heat removal, the thermal conductivity and thermal diffusion characteristics of graphene are not as good as we thought they would in practical application. There still remain gaps between the measured TC of single-layer graphene [2] and TC of graphene in devices, limiting the development of application.

We concentrate on graphene as the representative of two-dimensional materials because further understanding its thermal properties is of great significance not only for the breakthrough in theory but for practical application as well. Graphene has aroused researchers' enthusiasm for the heat dissipation

* Corresponding author (email: zhangg@ihpc.a-star.edu.sg, tianhe88@tsinghua.edu.cn, RenTL@tsinghua.edu.cn)

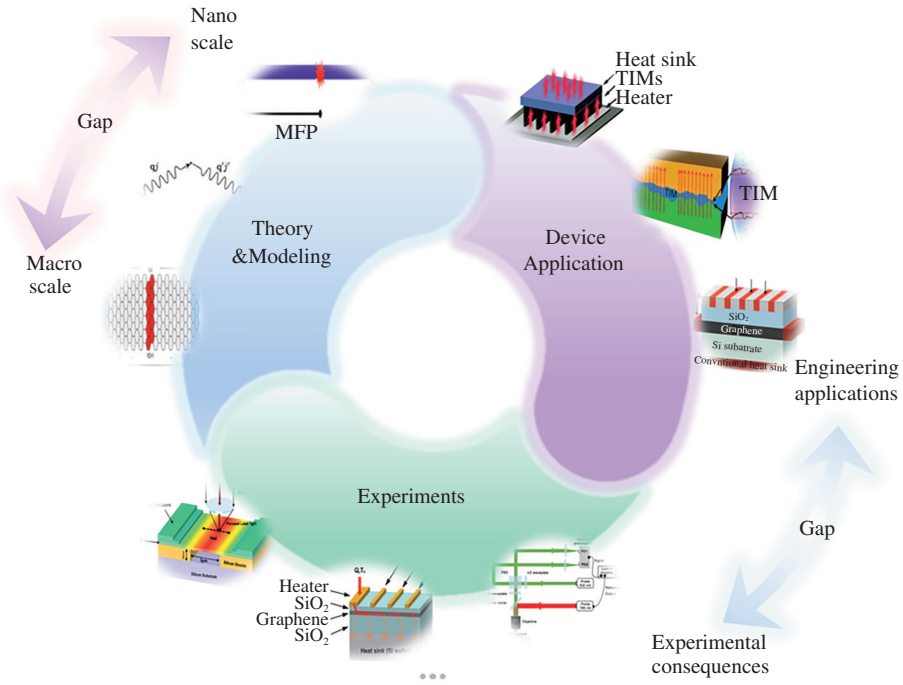

Figure 1 (Color online) Schematic of theory & modeling, experiment and device application of graphene. Gaps exist between theories of different scales and between experimental results and actual effect.

properties of two-dimensional materials. It is also the focus of application and the key to understanding various unique characteristics of 2D materials.

This review focuses on the excellent thermal properties of graphene and its state-of-art development and applications. In Sections 2 and 3, we introduce the basic theory of heat conduction in graphene and important simulation methods. Section 4 points out different experimental methods measuring the high TC of graphene. In Section 5, device applications of different forms of graphene are summarized, showing its outstanding heat dissipating capacity. Great attention is also paid to the existing drawbacks and gaps limiting graphene's thermal performance. In the final summary and prospect, we put forward and summarize two gaps lying between micro theoretical results and macro device applications. And higher actual heat dissipation capacity may be obtained through the change of morphology and structure of graphene material, or progress and breakthough in processing technology (Figure 1).

2 Basic theory

2.1 Fourier's law of heat conduction

The micro essence of heat transfer is that the energy of irregular thermal motion of molecules is transferred from high temperature objects to lower temperature ones by collision.

Fourier's law describes the principle of macroscopic heat conduction. The heat flux density is proportional to the temperature gradient. Owing to the limitation of temperature definition, in principle, Fourier's law of heat conduction is only applicable to steady temperature distribution in macro perspective, but it can also be used when the temperature changes slowly so that local thermodynamic state is equilibrium. Ideal pristine 2D structure cannot be obtained because of thermodynamic instability, so the thermal-conductivity divergence in 2D crystals needs to either limit the system size or introduce disorder to have the physically meaningful finite value of thermal conductivity [3]. For the validity of Fourier's law in low-dimensional systems, Ref. [4] provided a comprehensive summary.

Many theoretical models such as the harmonic chains model [5, 6], the FPU-β model [7, 8], the hard point gas model [9, 10], and some theoretical efforts such as the mode coupling theory (MCT) [8, 11], the renormalization group theory [12] and the Peierls-Boltzmann kinetic theory [13], have been conducted to study heat transport. These theories predict that the conductivity would diverge as a power law for 1D systems. For 2D cases, the MCT and the renormalization group theory predict logarithmic divergence [4].

The theory of molecular motion holds that the energy transport of gas is carried out by the collision of molecules. In a rough way, the heat conduction can be regarded as the result of position exchange of cold and hot molecules in a free range. According to the theory of molecular motion, the thermal conductivity of ideal gas can be deduced as

$$\kappa = \frac{1}{3}\rho c_V \overline{\lambda}\overline{v}. \tag{1}$$

The thermal conductivity of a solid is related to its composition and structure. For crystals, it is generally believed that it is contributed by both free electron and lattice heat conduction. The heat conduction in insulators and general semiconductors is mainly dominated by the lattice thermal conductivity. Based on the measured conductivity and using Wiedemann-Franz law, the electronic thermal conductivity is estimated to be less than 1% of the overall value [14]. Therefore, the thermal conductivity of graphene is mostly contributed by phonons, that are the main thermal carriers.

When the scale of heat transfer is close to the mean free path (MFP) of phonons, the local thermodynamic equilibrium state is difficult to achieve. When time criterion and space criterion of heat transfer become smaller, the non-Fourier effect is stronger. At room temperature, the coherent length of phonons in solid is about 1–10 nm, while the average free path of phonons is about hundreds nm [15]. When the sample size is less than the MFP of phonons in graphene, phonons transport is ballistic, instead of diffusive. When the size is further reduced to be shorter than the coherent length, the wave characteristic of phonons should be considered. Derived from the diffusion equation, the Fourier's law only applies when the size is much larger than MFP of phonons.

2.2 The various phonon scattering sources

In crystalline solids, the average phonon number satisfies the Bose Einstein distribution, which is positively correlated with temperature. Therefore, the average directional motion of phonon gas is generated on the basis of irregular motion, that is, phonon diffusion. Phonons are the energy quantum of lattice vibration in solids. The directional motion of phonons results in a heat flow. Therefore, the formula form of phonon thermal conductivity is similar to that of ideal gas, but heat carriers are phonons.

In principle, the strong C-C bond, light atomic mass and high atomic density are attributed to the high thermal conductivity in graphene. Moreover, monolayer graphene has three acoustic phonons and three optical phonons. Near the Γ point, the group velocity of ZA phonons is close to zero, and it is generally considered that the contribution to thermal conductivity is very small. On the other hand, the Hamiltonian of ideal graphene with single atom thickness along the X-Y plane is invariant along the Z-axis owing to the plane symmetry. These results in the scattering process exist only when even number of ZA phonons are involved. It leads to a significant increase in the relaxation time of ZA phonons in monolayer graphene, which makes an important contribution to the thermal conductivity. This is why the thermal conductivity of graphene decreases sharply from monolayer to bilayer. In practical applications, substrate or surface fluctuation caused by temperature effect will destroy the symmetry of plane inversion, which will reduce the contribution of ZA phonons to thermal conductivity [16].

The MFP of phonons is determined by two processes: one is the collision between phonons; the other is the scattering of phonons by defects in solid. In the harmonic approximation, there is no interaction between phonons. But when considering the anharmonic interaction, phonons may collide. For example, the third power term of potential energy in anharmonic interaction corresponds to a three phonon process, where two phonons collide to produce another phonon or a phonon splits into two phonons. If the momentum is conserve, the three-phonon process is called N-process. The N-process only changes the momentum distribution and has no contribution to the thermal resistance. If in a particular process the wave vector difference of the phonons before and after the collision is a non-zero inverted lattice vector, such a process is called umklapp processes (U-process) [17]. The U-process will make the phonon momentum change greatly, which will contribute to the thermal resistance.

In addition to collisions, defects exist in real solids, which also limit the phonon MFP, such as lattice defects, impurities, conduction electrons and interfaces [17–19]. The MPF λ of phonons scattered by boundaries or thermostats should be limited by the intrinsic phonon MFP λ_∞ in the bulk and the distance L between grain boundaries orthermostats [20] is shown as

$$\lambda^{-1} = \lambda_\infty^{-1} + L^{-1}. \tag{2}$$

Table 1 Summary of computational results of κ of graphene at room temperature (RT)

κ ($\mathrm{W{\cdot}m^{-1}\cdot K^{-1}}$)	Method	Comment	Ref.
∼2350	BTE	$L = 10$ μm	[21]
480–850	GK-MD	κ depends on stacking order	[22]
2000–5000	Valence force field, BTE	Strong width dependence	[23]
8000–10000	MD, Tersoff	Square graphene sheet	[24]

3 Theoretical methods to calculate thermal conductivity

When the material scale is reduced to micro scale, the Fourier law at macro scale is no longer applicable and the physical mechanism that dominates the heat conduction will also change greatly. The phonon properties can be predicted by many numerical methods, such as Boltzmann transport equation (BTE) method, non-equilibrium Green's function (NEGF) method and density functional theory (DFT). In this section, we introduce BTE method, NEGF method, molecular dynamics simulations and finite element method (FEM). The finite element simulation needs the input of material's intrinsic thermal conductivity, and temperature distribution of the object can be obtained after applying heat source and heat sink. For nanoscale materials, the intrinsic thermal conductivity can be calculated from the first three methods. In Table 1 [21–24], we present the room temperature thermal conductivity of graphene from these numerical studies.

3.1 BTE method

BTE describes the evolution equation of non-equilibrium distribution function, which can be used to derive the thermal conductivity of solids. The phonon thermal conductivity is determined from BTE [25–27].

$$\frac{\partial n_s(\boldsymbol{q})}{\partial t} + v \cdot \frac{\partial n_s(\boldsymbol{q})}{\partial x} = \left.\frac{\partial n_s(\boldsymbol{q})}{\partial t}\right|_{\mathrm{coll}}. \tag{3}$$

Callaway treated the U-process and N-process of phonon scattering separately and the thermal conductivity is obtained. Omini and Sparavigna [28] solved the linearized Boltzmann equation accurately by developing an iterative scheme. Based on the work of Omini and Sparavigna, Broido et al. [29] estimated the three-phonon scattering rates using Fermi gold rule and obtained an efficient iterative algorithm for solving BTE. In 2010, Broido et al. [21] adopted the scheme to explore phonon thermal transport in various solids including graphene. They found that out-of-plane polarized ZA phonons dominate the thermal transmission in graphene, which has a large density of states and heat capacity. In highly heat conductive materials with strong N-processes, the iterative scheme is more accurate than single-mode relaxation time approximation [30].

3.2 NEGF method

NEGF method can also provide theoretical prediction of the heat conduction of phonons [31]. In this method, the transmission function of the system can be computed by establishing the Green's functions built from the interatomic force constants of the system [32]. The heat flux and the thermal conductance can be computed using the Landauer formula [33],

$$J = \int \frac{\hbar\omega}{2\pi}\Xi(\omega)[n_1(\omega, T_1) - n_2(\omega, T_2)]\,\mathrm{d}\omega, \tag{4}$$

$$\kappa = \left|\frac{1}{T_1 - T_2}\int \frac{\hbar\omega}{2\pi}\Xi(\omega)[n_1(\omega, T_1) - n_2(\omega, T_2)]\,\mathrm{d}\omega\right|, \tag{5}$$

where n_1 and n_2 are the phonon occupation number at T_1 and T_2 respectively. So far, this method only uses the harmonic approximation force constant and can only calculate thermal conductivity in ballistic transport regime. The effects of grain boundary and the defects on thermal conductivity of graphene were explored by NEGF [34].

3.3 Molecular dynamics simulations

3.3.1 *Equilibrium molecular dynamics (EMD) method*

The Green-Kubo method uses the heat current fluctuations to calculate thermal conductivity κ based on the fluctuation-dissipation theorem, which is commonly employed in EMD simulation. Specifically, κ in the x direction can be computed as [35]

$$\kappa_x = \frac{1}{k_B V T^2} \int_0^\infty \langle J_x(t) J_x(0) \rangle \, \mathrm{d}t, \tag{6}$$

where k_B, V and J_x denote the Boltzmann constant, volume of the simulation cell and heat current in the x direction at time t. The formulation of Green-Kubo method indicates that thermal conductivity is time integral of heat current autocorrelation function. The results obtained can objectively reflect the intrinsic properties of the materials without the need for artificial heating bath. However, the simulation time appears to be a more significant consideration for EMD, where the convergence of correlation function is very slow and this method is only well suited to describe the properties of homogeneous systems [20].

3.3.2 *Non-equilibrium MD method (NEMD)*

There are two main ways to conduct non-equilibrium MD simulation. One is to impose a temperature gradient to generate a constant heat current and calculate thermal conductivity [36]. The other is disturbing the lattice sites to calculate thermal conductivity based on the linear response theory [37]. At present, most studies adopt the first method. High temperature and low temperature baths are applied at the boundary of the model to create temperature gradient and obtain a constant heat flow [38], which is described as NEMD. Müller [39] advanced a new method called reverse non-equilibrium molecular dynamics (RNEMD). In the simulation process, the velocity exchange between the atom with the highest velocity in the cold domain and the atom with the lowest velocity in the hot domain is carried out at regular intervals. The external heating flow is realized by atomic momentum exchange and the temperature difference is established, so it guarantees the conservation of momentum and energy.

BTE method and NEGF method can capture the thermal transport behavior from the phonon modes. BTE method treats the phonon as classical particle while NEGF method deals with the heat transmission of phonon from the interatomic force constants of the system by quantum mechanical. MD method simulates the movements of atoms instead of phonon transmission.

Commonly used MD method and BTE method are based on the classical mechanics. Owing to the Dulong-Petit limit, the heat capacity of classical mechanics deviates greatly from the quantum heat capacity when it is lower than the Debye temperature, while the two-dimensional materials such as graphene have high Debye temperature [40]. Additionally, the accuracy of MD method is limited by the empirical interatomic potential used. MD is widely used in thermal conductivity simulation of graphene for having no thermodynamic assumption, and it can also simulate the experimental environment [41] and complex structure, such as the thermal transport in superlattices [42].

3.4 FEM

Numerical simulation technology is usually used to study "field" problems, including displacement field, stress field, electromagnetic field, temperature field, flow field, and vibration characteristics. The problems studied can be summarized as solving the governing equations (ordinary differential equations or partial differential equations) in given conditions. At present, the most widely used numerical simulation method is FEM. It is a numerical analysis technology which combines theory, calculation and computer software.

FEM regards the solution region as composed of many small subdomains connected at the nodes. The quantity of the interior points can be obtained by the selected functions that interpolate at grid points. Because of the simple shape of the element, it is easy to establish the equation between the model and the quantity at nodes, and the model gives an approximate solution of the basic equation in subdomain. Meshing is an important part of establishing finite element model. The finer the element partition is, the more accurate the calculation results will be. However, if the mesh density is too large, the calculation time will be greatly increased but the calculation accuracy will not increase proportionally, so two factors must both be considered when determining the mesh quantity. In addition, grids of different sizes are used in different parts of the structure. For example, in thermal analysis, the parts with large temperature

gradient need to use dense mesh while the sparse mesh should be divided when temperature gradient is smaller. FEM is suitable for complicated geometry, complex materials and complicated boundary conditions.

In 1943, Courant [43] proposed an approximative method in his mathematic paper which is similar to FEM. Clough [44] used the name "finite element method" in his paper on plane elasticity in 1960. With the development of computer and software, FEM ushered in faster development after 1970. With heat conduction equation as its governing eqution, finite element thermal analysis is used to calculate the steady or transient temperature distribution, heat gain or loss, temperature gradient and heat flux. Compared with atomistic modeling, the main advantage of the FEM is that systems of the FEM are at macroscopic scale over long periods while the atomistic modeling is at nanoscale for a short time. The thermal conductivity of individual material provided by atomistic simulations can be applied to the FEM to simulate the overall thermal property of the system [45], and FEM is often used to predict the heat dissipation effect of the thermal conductive devices. This is irreplaceable by atomistic simulation. To pass the limits of methods at different scales and obtain more accurate simulation results, multiscale modeling method should be developed which combines FEM and atomistic simulations such as MD.

4 Experimental measurement

The chief methods of measuring the thermal conductivity of solids can be grouped into two categories: steady-state method and transient plane source method (TPS) [3]. In steady-state method, thermocouples are widely utilized. The samples are heated up by electrical means providing power until they eventually reach the steady state, and their relevant parameters are then measured by other techniques. However, problem arises with merely measuring the temperature gradient produced by a steady flow of heat in a one-dimensional geometry when it extends to a higher temperature, as a large amount of heat is radiated away through the process of heat conduction [46]. In order to deal with that problem, transient method, for example, the transient 3ω technique for thin films [3, 46], is developed to eliminate those difficulties. By recording the thermal gradient as a function of time, the TPS method is more accurate and efficient compared to traditional ways of measurement, enabling researchers to test the thermal conductivity of dynamic materials of different shapes.

Based on the fundamental principles of the two chief methods of measurement of thermal conductivity, some specific techniques are invented and applied in the experimental study of thermal conduction in graphene. Up to date, there are about ten thermal characterization methods applied in the measurement of thermal conductivity of graphene, some of which are given in Figure 2, whereas different techniques give very different results even for the same material, so the technique is selected in terms of the geometry and required properties of the materials [47]. The experimental results of thermal conductivity of graphene from published studies are given in Table 2 [2, 14, 48–53].

In this section, we mainly focus on the optothermal Raman spectroscopy technique, which has been used for measurement of thermal conductivity of a wide range of 2D materials, including various kinds of graphene films [47]. We will also talk about the heat spreader method, which can be perceived as a form of 3ω method and which is a widely used technique for thermal conductivity measurement on bulk and thin film [54, 55]. From the discussion of the methods above, we can get a more comprehensive thinking of experimental measurement of thermal conductivity of graphene and 2D materials.

4.1 Optothermal Raman spectroscopy technique

The first experimental study of thermal conductivity of graphene was probably launched by the development of optothermal Raman spectroscopy technique [3], which is a direct steady-state method popularized by Balandin and his coworkers in their study [2]. The preconditions of this methods can be concluded into two aspects: establishment of the temperature dependence of Raman peak, production of local heating on tested sample [2], as shown in Figure 3. As for the first step, it is done by the low-power laser excitation to prevent the local heating of the sample, and the temperature dependence of Raman peak is utilized to determine the local temperature [47]. As for the second step, by focusing the excitation laser light on the middle of the suspended SLG, which creates a hot spot that generates heat wave spreading towards the heat sinks at the end of the SLG, scientists are able to detect a mild power dissipation in the device [2]. In Balandin's work, the original detection of thermal conductivity of graphene was deduced from the comparison of the measured integrated Raman intensity of G peak of the graphene and

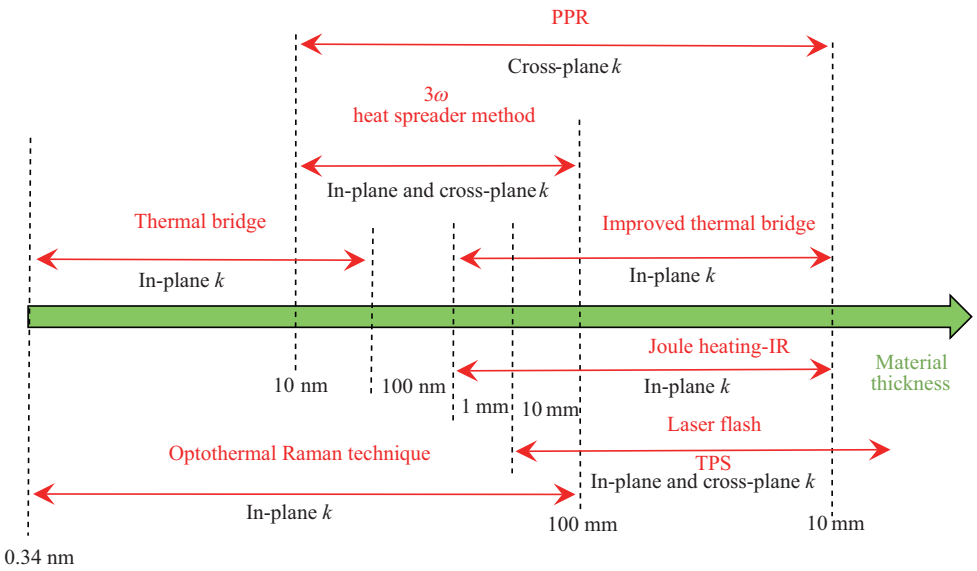

Figure 2 (Color online) Methods used for measurement of thermal conductivity of 2D materials [47].

Table 2 Summary of TC of graphene in experiments

κ ($\mathrm{W\cdot m^{-1}\cdot K^{-1}}$)	Method	Material type	Ref.
$\sim (4.84 \pm 0.44) \times 10^3 - (5.30 \pm 0.48) \times 10^3$	Optothermal Raman spectroscopy technique	Suspended exfoliated single-layer graphene (SLG), room temperature (RT)	[2]
$\sim$ 3000–5300		Suspended exfoliated SLG, RT	[48]
$\sim$ 3080–5150		Suspended exfoliated SLG, RT	[14]
$\sim$ 1500–5000	Optothermal Raman spectroscopy technique + electrical burning	Suspended chemical vapor deposition (CVD) graphene, RT	[49]
$\sim$ 2500	Optothermal Raman spectroscopy technique	Suspended CVD graphene, 350 K	[50]
$\sim$ 1400		Suspended CVD graphene, 500 K	[50]
$\sim$ 630		Graphene membrane, 600 K	[50]
below 160	Heat spreader method (3ω method)	Exfoliated SLG encased within silicon dioxide, RT	[51, 52]
$\sim$ 7000 (crude estimate)	All electrical, 3ω method	Substrate-supported CVD graphene, RT	[49]
$\sim$ 600	Thermal bridge	SLG exfoliated on a silicon dioxide support	[53]
$\sim$ 370	Laser heating	Exfoliated graphene supported on SiO_2, RT	[50]

graphite [2, 47], and this method was modified to measure the power dissipation by means of a detector under the sample [3].

In the first experimental study of the thermal conductivity of graphene, the research demonstrated that SLG has an extremely high thermal conductivity up to about 5000 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ at room temperature [2]. Similar non-contact optical techniques were utilized in other researches, which eventually came to the same conclusion that graphene reveals unusually high thermal conductivity at room temperature [14, 48, 49]. For higher temperature, another research repeating the same method drew the conclusion that the thermal conductivity of the suspended graphene exceeded 2500 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ near 350 K and dropped to 1400 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ at 500 K [50]. It was found by another group that the thermal conductivity reached 630 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ at an even higher temperature of 600 K [56].

With respect to its easy sample preparation, high accuracy and freedom in material size, optothermal

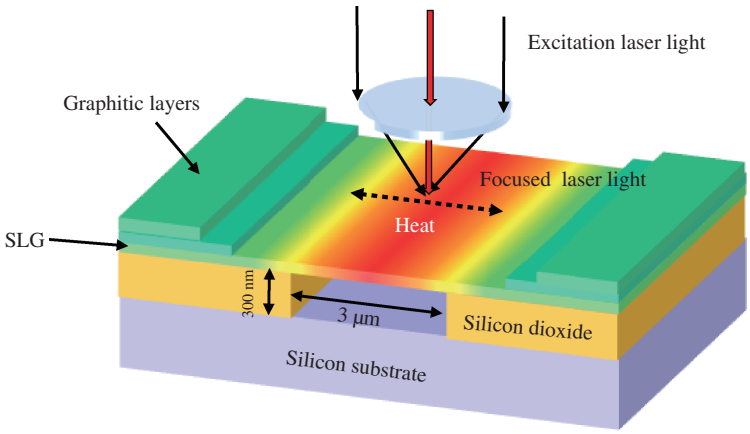

Figure 3 (Color online) Schematic of the experiment showing the excitation laser light focused on a graphene layer suspended across a trench. The focused laser light creates a local hot spot and generates a heat wave inside SLG propagating toward heat sinks [2].

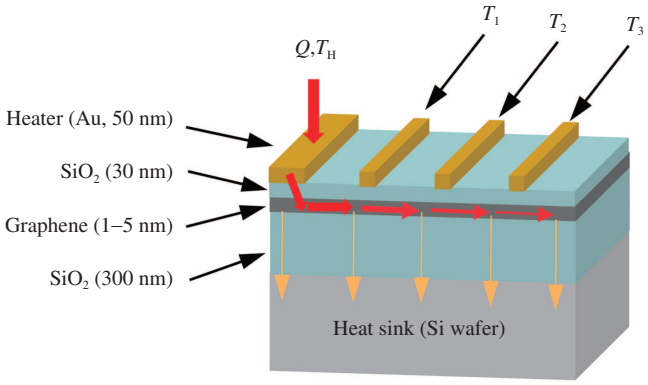

Figure 4 (Color online) Schematic of the "heat spreader method" to measure the in-plane κ of graphene encased in a film of SiO_2 [51, 52].

Raman spectroscopy technique can be not only applied in measuring the in-plane thermal conductivity of single-layer graphene (SLG), but also extended to an even wider range, including other materials like MoS_2 [57], as well as relatively thick films like free-standing reduced graphene oxide (rGO) films [54]. However, its calibration coefficient at different temperature has non-negligible difference, making the data less credible to some extent [47]. It also has difficulty in measuring the thermal conductivity of atomically thin materials, considering its complex sample preparations at such a scale.

4.2 Heat spreader method-3ω method

By using optothermal Raman spectroscopy technique, we can get relatively accurate data of the thermal conductivity of the suspended graphene. But for practical use, we need to find ways of measuring the thermal conductivity of encased graphene or supported graphene. As the measurement of thermal conductivity of encased graphene is more challenging owing to the lack of direct access [55], new techniques are in urgent need for the detection of thermal conductivity.

As is shown in an independent study, the authors [51,52] adopted a heat spreader method to study the heat dissipation performance of encased graphene. By dissipating heat at a constant rate from a metallic line heater, the heat can spread laterally through the graphene layer encased between SiO_2 layers, while flowing simultaneously through the stack into Si heat sink (Figure 4). The temperature is detected by three temperature sensors and is later fitted by a numerical model to get the thermal conductivity of encased graphene. It is found that the in-plane thermal conductivity of encased graphene sheets is much lower than that of the freely-suspended graphene sheets tested by Balandin [2, 51, 52], as the in-plane thermal conductivity of SLG encased within silicon dioxide is tested below than 160 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$.

The method adopted in this research is definitely an application of 3ω techniques. As for this method, diverse from other measurements whose heat is applied as a known rate and temperature is detected to

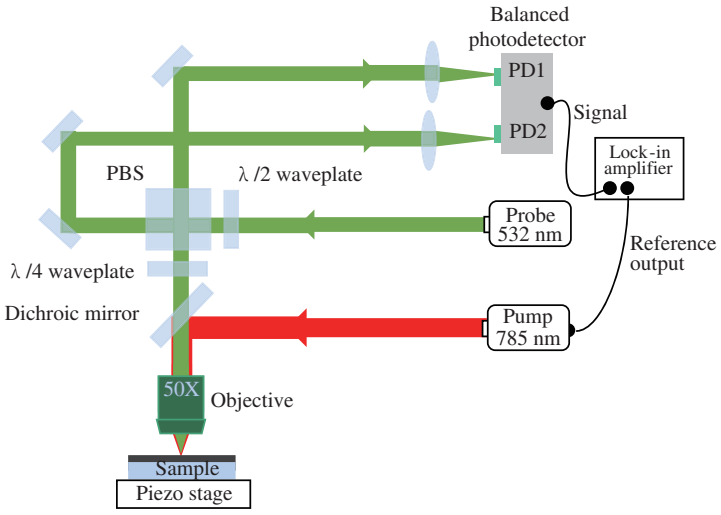

Figure 5 (Color online) Schematic of our FDTR micro-scope. A digitally modulated pump laser heats the sample while a probe beam monitors the surface reflectivity. A balanced photodetector is used to improve the signal to noise ratio. A piezo stage is used to scan the sample for imaging [55].

acquire the thermal conductivity, the heater and the thermometer are integrated in a deposited wire in this measurement [47]. In order to get a more accurate record of the thermal conductivity of thin film on substrate and satisfy the assumption this method makes, the targeted materials need to meet several requirements of size: an appropriate wire width larger than the film thickness and smaller than the thermal penetration depth [47]. Moreover, the substrate requires a higher thermal conductivity than the film and the heat conduction across the film needs to be 1D [47]. Under these circumstances, researchers can easily get a high accurate information of both the in-plane and cross-plane thermal conductivity of supported or encased graphene at a low cost. However, compared to the data obtained from other methods, the thermal conductivity of substrate is usually lower, especially in the thin film measurement [47, 53].

4.3 Other methods

Despite the techniques that mentioned above, there are also various techniques utilized in measurement of the thermal conductivity of graphene and 2D materials. Ref. [53] adopted a thermal bridge method to find similar consequences that in-plane thermal conductivity of supported graphene on Si/SiO_2 is much lower than that of the suspended graphene, with a value of 600 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature, but is still much higher than most of the metals. It has also been adopted in [58] to study the thermal conductivity of graphene. As a method first is applied in the measurement of the thermal conductivity of carbon nanotubes, it has now been regarded as one of the most successful methods in measuring the thermal conductivity of 2D materials, nanowires and nanotubes [47, 59]. However, it faces the challenge stems from the unavoidable influence of thermal conductance [47].

Another study had described frequency-domain thermore-flectance (FDTR). As shown in Figure 5, FDTR is based on the time-domain thermore-flectance (TDTR) method to image graphene samples encased by Ti and SiO_2, which found that Ti has no significant impact on the thermal conductivity of graphene exfoliated on SiO_2 [55]. Besides this, researchers have also developed other techniques such as Joule heating-IR, laser flash, pulsed photothermal reflectance (PPR), etc [47].

The study of heat dissipation in graphene has shown the intrinsic thermal conductivity of graphene is considerably high [2, 14, 48, 49]. However, in application of graphene materials, defects, impurities and many other extrinsic factors exert great influence on the graphene's heat dissipation performance in devices, which do not exhibit the high values it has in experiments [3]. Inside the graphene lattice, both the defects and impurities between atoms may block the heat transfer to some degree, which further lead to the decrease in the value of thermal conductivity of graphene. The different interface structure caused by grain boundaries and substrate coupling will also lead to the alteration of thermal conductivity of graphene, determined by the types of substrates and interface resistance.

Nevertheless, graphene with defects and impurities is usually not taken into consideration in most of the techniques. Even though some studies have considered the thermal conductivity and the heat

dissipation performance of encased graphene in different materials [51, 52, 55], the graphene layer is a combination of perfect SLG, lacking defects or impurities. As a consequence of the absence of relevant studies, it cannot represent the thermal conductivity of devices as well.

Besides, it is also proposed that the processing largely brings to the vast difference in thermal conductivity of graphene. This can be deduced from the fabrication of graphene nanoplatelets (GNPs). In Fukushama's work, a special treatment was invented to exfoliate graphite flakes by using tetradecyl amine to intercalate graphite to prepare for the graphene [60]. Apart from this method, graphene can also be produced by using $FeCl_3$ [61] to intercalate graphite. According to the relevant data in these two researches, the graphene intercalated by tetradecyl amine has a higher specific surface area than that intercalated by $FeCl_3$, and the thermal conductivity of GNPs fabricated by using tetradecyl amine as intercalation agents has improved 152.7%, compared to 142.3% by using $FeCl_3$ as intercalation agents [60,61]. As a consequence, the graphene intercalated by tetradecyl amine illustrates superiority in enhancing the thermal conductivity of GNPs to those intercalated by $FeCl_3$ at a lower volume fabrication. However, the significant discrepancy of thermal conductivity of graphene on account of the processing is usually not taken into consideration in most of the techniques as well.

Moreover, though there are diverse methods of measuring the thermal conductivity of graphene, none of these methods are completely applicable to all the materials in different conditions. Generally speaking, the entire experimental process is required to follow relevant theoretical modeling. For example, in the optothermal Raman spectroscopy technique, the materials under study need a pronounced Raman peak established by low power laser excitation [47]. The rigorous limitations improve the reliability of studies, but they restrict the research of graphene applied in devices meanwhile.

Therefore, the limitations of different techniques we use restrict its development in relevant devices, giving rise to the gap between experimental work and engineering applications. In order to get high quality graphene films, the comparison and combination of different techniques may be the future potential subjects, and techniques utilized to measure the thermal conductivity of defective graphene or other similar models are in urgent need in the next phase of related research.

5 Device applications

For the reason that graphene could be produced on a large scale and possesses exciting and outstanding thermal properties, it has a good prospect to use graphene as heat spreaders and to break through the bottleneck caused by heat dissipation problems in the integrated electronics industry. The ultra-high TC is beneficial for the cooling of electronic devices and indicates its applicability for thermal management. By introducing isotopes, vacancies, substrates, strain and so on, phonon scattering process will be enhanced, so will the heat conductance. However, these methods only affect phonons with short wavelength, and phonon manipulation still remains a difficult task [62]. Another way to control heat transport is to apply extrinsic field. Although heat flux, not as electric current, is difficult to be controlled directly by electromagnetic field, it still can be manipulate by extrinsic field. Liu et al. [63] demonstrated that partially clamped SLG could serve as a thermal rectifier. The distance between clamp and graphene is controlled by applying external pressure to further control the heat flow [63]. Using MD simulations, Xu et al. [64] showed a nonnegligible interfacial thermal resistance between suspended and encased SLG by introducing inhomogeneous external perturbation. The exploration of different external fields and different structures will bring brighter application prospects to this method. In addition, graphene can also solve problems in optoelectronics, photonics, bioengineering and so on, which greatly expands its scope of application. In energy devices, it can serve as an active medium or transparent electrode and it also plays its part in supercapacitors and thermoelectric materials [65, 66]. Many simulation and experimental researches have been carried out and most of the studies have reported promising results. In this section, we review the effect of different kinds of graphene applied in multiple devices and also pay attention to the gap for graphene applications.

From Sections 3 and 4, we know that the thermal conductivity of single-layer suspension graphene obtained by simulation and experimental measurement is very high, reaching 5000 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [2]. However, it is just an ideal state of thermal conductivity ignoring lots of influence factors. In practical application, graphene is usually more than one layer and needs to be bonded to the substrate, which will significantly reduce the TC of graphene for about one or two orders of magnitude. The decrease in TC is probably due to the influence of interface interaction and defects and so on. Even so, compared with

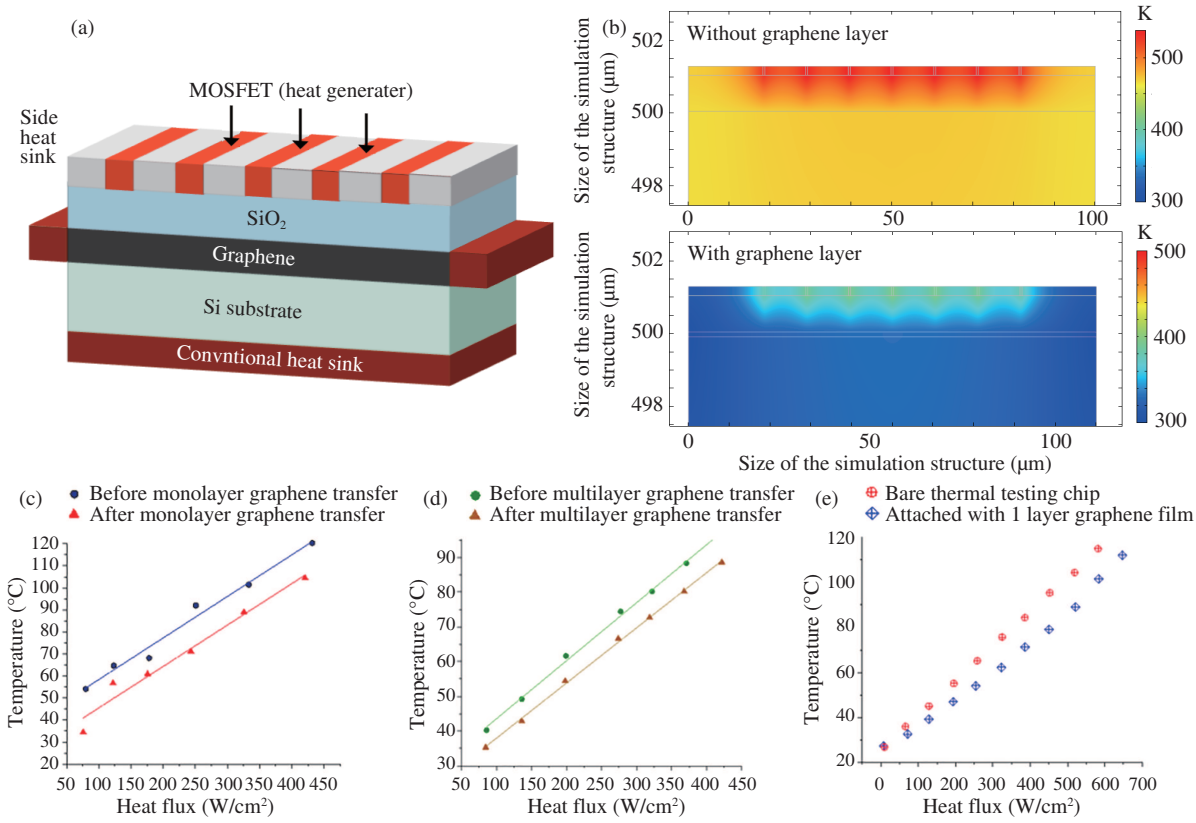

Figure 6 (Color online) (a) Schematic of the simulation structure. The thicknesses are not to scale [69]. (b) Temperature distribution obtained by finite element simulation. (c)–(e) Hot spot temperature before and after graphene is transferred onto the chip with the data from [72, 76].

the TC of metal films or other thin film materials, TC of graphene combined with the substrate is still rather high [67, 68]. It still plays an important role in reducing the overheat damage and improving heat dissipation in devices.

5.1 Graphene films

Owing to graphene's high in-plane TC, feasibility studies of graphene applied as lateral heat spreaders to solve the hot-spot problems have been carried out. Subrina et al. [69] sandwiched a graphene layer in silicon-on-insulator (SOI) circuits, attaching graphene's two ends to side heat sinks (Figure 6(a)). It turned out that the introduction of graphene film can lead to tremendous reduction in temperature of the hot spots [69]. Corresponding simulation result is shown in Figure 6(b). Zhang et al. [70] demonstrated that by using graphene-based films as a dielectric, the hot spot temperature decreased by 6°C when heat flux was 1200 $\mathrm{W \cdot cm^{-2}}$. Apart from simulation work, experiments are also in progress. Gao et al. [71] introduced the monolayer graphene heat spreader to Pt micro-heater embedded chip and found that when the heat flux reached 800 $\mathrm{W \cdot cm^{-2}}$, the hot spot temperature was decreased by 5°C. This result was further improved in their follow-up studies, as shown in Figures 6(c) and (d) [72]. Shih et al. [73] capped graphene on the surface of a photonic crystal cavity, reducing the thermal resistance by more than half and lowering the temperature by 45 K for an optical power of 100 μW. Study by Zhang et al. [74] showed that the functionalization of graphene-based film with silane molecules could double its heat spreading ability. Compared with 6°C drop using graphene heat spreader without silane functionalized graphene oxide (FGO), the functionalized film could decrease the hot spot temperature by 12°C [74]. Han et al. [75] demonstrated that the embedded graphene oxide in a gallium nitride light emitting diode (LED) could alleviate self-heating problems, enable LED to give out brighter light. Huang et al. [76] used a thermal testing chip attached with monolayer graphene film and got decreased and more uniform temperature (Figure 6(e)). Although TC of graphene in radiator is not as high as that of perfect graphene layer owing to the interaction with interfaces, it is still higher than the TC of traditional metal films. In a

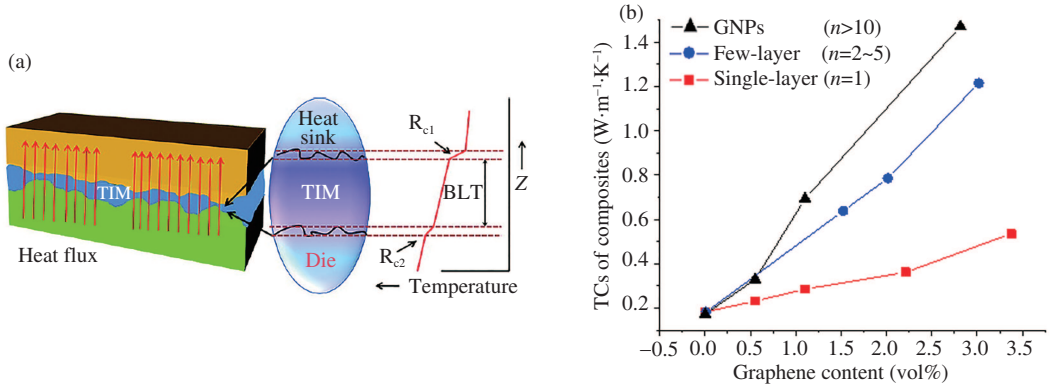

Figure 7 (Color online) (a) Demonstration of principle of TIM [80] @Copyright 2020 the American Chemical Society. (b) Composites' TC with different graphene layers, with data from [89].

hot-spot test in chip-on-film packaging, Bae et al. [77] found a better performance of graphene film in heat distribution than a gold layer under the same condition. By using graphene film heat spreader, the heat generated at the hot spot is more evenly distributed and propagated onto larger area, which increases the uniformity of heat flux crossing the devices, thus avoiding thermal damages caused by increased input power and achieving better performance and longer lifetime.

However, even though graphene displays great properties as heat spreader and outperforms many other thermal materials, we can still see from the experimental data that its thermal conductivity is about one order of magnitude smaller than that of single-layer graphene in experimental measurement, which greatly limits its performance as a heat dissipation material. Further development may lie in the improvement of processing and morphology. A novel p-n-p thermal management design was put forward by Lee et al. [78], who placed graphene heat spreader at the backside of GaAs/InGaAs/InGaP collector-up HBTs, reaching an over 30% reduction of thermal resistance. There were also studies indicating that better performance may be achieved by improving the adhesion between graphene and insulator, increasing the thermal contact between graphene and substrate, minimizing the film thickness and orientating more orderly [70].

5.2 Graphene composite materials

Recent years have witnessed the fast development of various kinds of graphene-related materials and the exploration of combining graphene with many other things. Among these multiple thermal conductive materials, polymer matrix composites stood out for its outstanding properties, such as being lightweight, exhibiting good corrosion resistance, easy to process, etc [79]. Graphene, with its high TC, has proved itself to be a good filler, improving the thermal properties of polymers. Nowadays, graphene-polymer composites play a more important role in heat conduction application.

With the advent of 5G era, power density of high-performance chips is reaching a grand new level, which calls for better thermal interface materials (TIMs) (Figure 7(a) [80]) bringing more efficient heat diffusion. However, traditional commercial TIMs have relatively low TC, most of which is less than 5 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$. When combined with graphene material, the situation could be greatly improved. Shtein et al. [81] reported a dispersion of GNPs in a polymer matrix, increasing the TC by more than 60 times compared with neat polymer. Yavari et al. [82] added graphene platelets to organic phase and found it leading to about 140% increase in TC. Apart from bringing new development to TIMs, graphene-polymer composite also has other applications. Ji et al. [83] demonstrated that embedding ultrathin-graphite foams in a phase change material (PCM) can increase its TC by 18 times, which helps to achieve the high power capacity targets of thermal storage applications such as solar thermal harvesting and electronic devices' thermal management. Similarly, Mehrali et al. [84] showed that composite PCM prepared using paraffin and graphene oxide sheets had a highly improved TC. In addition, graphene composites can also function as good heat sink materials. As early as 2003, Norley et al. [85] has proposed a graphite composite heat sink with anisotropic heat conduction. In recent years, Hsieh et al. [86] decorated graphene nanosheets with Cu and found an increase in TC of the heat sink as the loading increases, reaching 1912 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ at 50°C. Hu et al. [87] coated graphene nanosheets on Al heat sink and achieved temperature reduction by 5°C at a heat flux of 1.8 $\mathrm{W\cdot cm^{-1}}$.

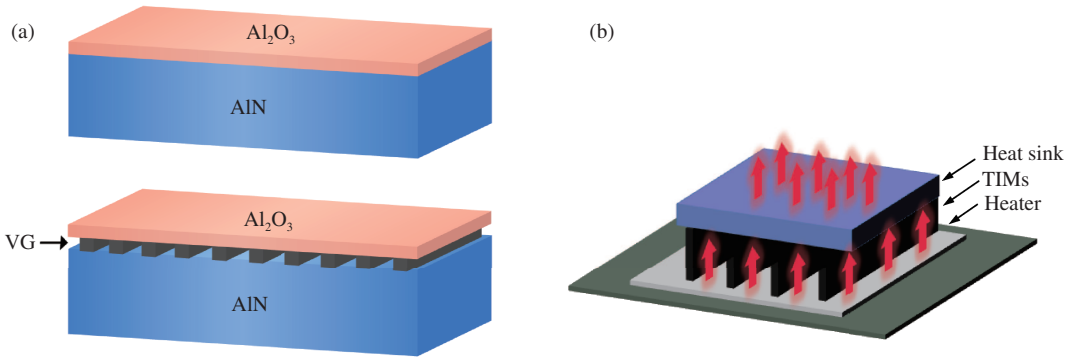

Figure 8 (Color online) Simulation models of vertical graphene (a) nanowalls [93] and (b) arrays [94].

Many factors affect the thermal performance of graphene-polymer composites, one of which is morphology. Chu et al. [88] observed an enhancement of TC in two types of wrinkled GNPs and introduced the waviness factor to analyze TC affecting by waviness effect. Shen et al. [89] found in simulation that the TCs across the graphene/epoxy interface increased when the number of layers increased, as shown in Figure 7(b), indicating a good perspective to apply multilayer graphene in composites and to bring high TCs and possibility of better thermal management.

5.3 Graphene material in 3D structure

High heat removal efficiency has become a critical aspect for miniaturized next-generation electronic devices. With the increasing integration level of devices, heat dissipation is needed not only in different positions but in different directions as well. Graphene layers can effectively spread the heat flux in the plane for its ultrahigh in-plane thermal conductivity, preventing the sever hot-spot problem. However, when it comes to the cross-plane direction, graphene film cannot perform well. The unique two-dimensional structure of graphene, the chemical bond in the plane and van der Waals force between layers, make the thermal conductivity of graphene significantly anisotropic. This leads to rather low TC in the out-of-plane direction, which is a huge drawback in its thermal performance, especially when applied in devices with 3D structures requiring heat dissipation in all directions. It is an urgent problem because nearly under all circumstances, it is essential that heat propagates across the plane efficiently and is carried away after reaching the heat sink. Phonon bridge mechanism is widely used to solve this problem, enhancing interfacial heat transfer [90]. Using MD method, Liu et al. [91] found that total heat current in the out-of-plane direction was increased by about 50% through junctions, which are covalent cross-linkers between GNRs. Ong et al. [92] proposed that tensile strain loading of graphene/h-BN can improve the alignment of out-of-plane phonon modes, thus improving the interfacial thermal conductivity significantly. In recent years, graphene-based 3D materials have gradually become the protagonist of the new trend of development.

Ci et al. [93] found that vertical graphene (VG) nanowalls can enhance the heat conductance in vertical direction from AlN film to substrate, resulting in a 3.8% temperature reduction, which suggested that VG nanowalls can act as a good buffer layer and remove excessive heat efficiently (Figure 8(a)). Xu et al. [94] showed that the introduction of VG arrays between a ceramic heater and a commercial heat sink would make the maximum temperature 10°C lower than the temperature we got when thermal conductive tape was used (Figure 8(b)). Liang et al. [95] assembled functionalized multilayer graphene sheets vertically between the contact Si/Si surfaces, getting a 3D structure with relatively high equivalent TC of 75.5 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ and low thermal resistance. Almost all the literatures indicate great potential of VG for electronic cooling applications. Another three-dimensional structure of graphene, graphene foam, has porous foam-like structure and shows the potential as TIM material, with its thermal conductivity reaching 88 $\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ [96]. In 2017, Zhamu et al. [97] provided a method to create integral graphene carbon hybrid foam, which also expands graphene foam's application as heat sink.

6 Prospect

According to the order of this review, we propose and emphasize the following gaps.

(1) The first is the gap between heat conduction theories on nanoscale, microscale and macroscale. In Section 2, we point out that the heat transfer theories on the macroscale have been well established but some are no longer applicable when applied to smaller scale owing to the change of the scale and limitations of the theory. Section 3 puts forward that different modeling methods have different application scope and characteristics, and cross scale simulation method is the direction we should develop to obtain more accurate simulation results.

(2) The second is the gap between fundamental and engineering application. The experimental measurement of TC of suspended SLG is indeed ultra-high. However, defects, impurities and many other factors have great influence on graphene material applied in devices. In Section 4 we propose that the influence that processing brings to the quality of the material plays a much important role in graphene's heat dissipation performance than its high intrinsic TC. Differences still exist between theoretical simulation prediction and actual effect. Section 5 points out that this is an urgent problem.

Since 2004, graphene has been studied in an endless stream. With the improving demand in emerging industries and devices being increasingly more integrated and miniaturized, graphene as a thermal conductive material with novel properties is likely to be required more widely [98, 99]. So there is still lots of room for further development and novel applications. As for progress that has been made, there are many researches on graphene, including but not limited to the discussion of nanoscale heat transfer theory, the calculation of TC of different graphene forms, and the simulation of heat dissipation effect of graphene in devices. Exploration in fields beyond heat transfer has also been carried out, such as absorption [100], mechanical and photoelectric characteristics. Good results have been obtained. However, the excellent thermal properties of graphene could not be fully demonstrated in real devices because of defects, substrates, interfaces and other factors influencing graphene film's thermal performance. Recently, progress has been made and graphene is playing an increasingly important role in microelectronics industry. Huawei has applied graphene film as heat dissipation material in Mate 20X in 2018, realizing its commercialization. And Xiaomi released Mi 10 with three-dimensional cooling system composed of graphene in February 2020. We will not stop pursuing better thermal performance and device cooling effect. Therefore, how to fill the gaps mentioned above, how to make the unique properties of nanoscale reflected in the macroscale and how to give full play to graphene's excellent heat dissipation capacity are still the key problems that need to be solved. These are of great significance for the field of micro and nano devices and can bring huge changes to our daily life. Production of graphene in large quantities with high quality by low cost is an important prerequisite for its commercial application [101]. And changing the morphology and structure and improving the processing technology may be the direction of research and development to obtain higher heat diffusion effect.

The age of "graphene plus" is losing its vitality. The creation and preparation of new forms of graphene are developing as a new trend. With further development, the location, application scenarios and requirements of thermal materials will be increasingly diversified. For example, for chips, good heat dissipation materials both on and off chip are needed and both longitudinal and transverse heat transfer are required. Therefore, different forms of graphene are demanded to better fit different conditions. It will be very useful and enlightening to summarize the characteristics of different forms of graphene and establish a table to find suitable graphene materials and achieve the best match.

We are achieving goals, though there is still long way to go before reaching excellent device cooling performance. We believe that with the continuous development of new forms of graphene, with the expansion of dimensions, with the better combination of nano, micro and macro scope, graphene materials will have better application performance, and one day will bring subversive development for the microelectronics industry.

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