Thermoelectric transport in graphene and 2D layered Materials

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ABSTRACT

In early 90s, Hicks and Dresselhaus proposed that low dimensional materials are advantages for thermoelectric applications due to the sharp features in their density-of-states, resulting in a high Seebeck coefficient and, potentially, in a high thermoelectric power factor. 2D materials are the latest class of low dimensional materials studied for thermoelectric applications. The experimental exfoliation of graphene, a single-layer of carbon atoms in 2004, triggered an avalanche of studies devoted to 2D materials in view of electronic, thermal and optical applications. One can mix and match and stack 2D layers to form van der Waals hetero-structures. Such structures have extreme anisotropic transport properties. Both in-plane and cross-plane thermoelectric transport in these structures are of interest. In this short review article, we first review the progress achieved so far in the study of thermoelectric transport properties of graphene, the most widely studied 2D material, as a representative of interesting in-plane thermoelectric properties. Then, we turn our attention to the layered materials, in their cross-plane direction, highlighting their role as potential structures for solid state thermionic power generators and coolers.

Keywords: Thermoelectric, Thermionic, 2D van der Waals heterostructures, Graphene

1. Introduction

In 1821, Seebeck observed deflection of a magnetic needle when a part of his electrical circuit was heated. Charge carries diffuse from the hot side to the cold side generating a voltage difference when there is a temperature difference. The ratio of the voltage generated to the applied temperature difference is called the Seebeck coefficient. Thermoelectric modules are working based on the Seebeck effect. They are made out of a series of n-type and p-type legs thermally in parallel and electrically in series. Thermoelectric modules can work in three distinct modes of operation: power generation mode, Peltier refrigeration mode, and active cooling mode. The power generation mode is based on the Seebeck effect. In this mode, heat is converted to electricity. In the refrigeration mode, electricity is used to pump heat from a cold source to a hot sink. Finally, in the active cooling mode, electrical current is reversed to pump heat in its natural direction and from hot to cold. For the first two modes of operations, materials with large thermoelectric figure of merit ($ZT = \frac{\sigma S^2 T}{\kappa}$) are desirable where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and κ is the thermal conductivity. [1] However, in the last mode of operation, i.e. active cooling, where the aim is to simply cool down a hot object in a fast and efficient manner, materials with large thermoelectric power factor ($PF = \sigma S^2$) and large thermal conductivity are needed. In this mode, the direction of heat flux is from hot (hot object) to cold (ambient) which is the natural heat flux direction. A large thermal conductivity enables efficient passive cooling (heat conduction) and a large power factor enables efficient active cooling.[2] Considering the Joule heating, the Peltier current and the heat conduction, the heat flux pumped from the hot side to the cold side could be optimized with respect to the electrical current. The resulted optimum heat flux extracted from the hot side could be expressed as $Q'_{max} = (\frac{PFT_H^2}{2\Delta T} + \kappa)\nabla T$, where T_H is the temperature at the hot side, and ΔT is the temperature difference between the hot side and the cold side. The term in the parenthesis is the effective thermal conductivity wherein the first term is the active thermal conductivity (proportional to the power factor) and the second term is the passive thermal conductivity (from passive flow of phonons and electrons under zero electrical current). [2] Figure 1 shows the effective thermal conductivity as a function of temperature difference (ΔT) divided by absolute temperature at the hot side. Curves are plotted for $\kappa = 1\ W/mK$, which is the typical value of the state of the art thermoelectric materials and for different ZT values. While a high ZT results in enhanced effective thermal conductivity, it is not enough to reach to competitive thermal conductivity values comparable to the best passive thermal conductors such as copper and diamond. While κ could be enhanced by two orders of magnitude, when ZT is large, since the start point is low, the final achieved thermal conductivity is still small. Alternatively, if the lattice thermal conductivity is around 100 W/mK, even a small ZT of 0.5 can enhance the effective thermal conductivity to values larger than copper and diamond. Note that a ZT of 4 has been a dream for more than a century. On the contrary, there are currently materials available (such as cobalt[3] and PdAg [4]) that are very close to the second case scenario of high thermal conductivity and modest ZT values. Also note that this second class of materials have not been targeted in the past and have been overlooked.

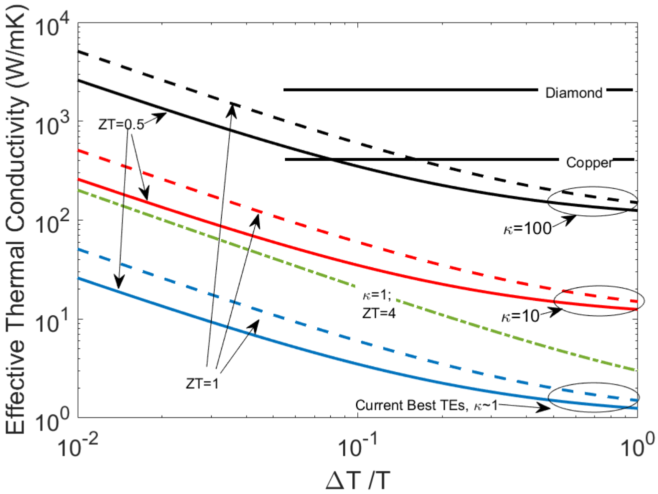


Figure 1. Effective thermal conductivity as a function of temperature difference divided by temperature at the hot side. Curves are plotted for materials with passive thermal conductivity, κ, of 1, 10 and 100 W/mK and ZT values of 0.5, 1 and 4. Effective thermal conductivity is a sum of passive and active thermal conductivity at the optimum current.

By 1960, most of today's commercial thermoelectric materials were identified. They were mostly Bi_2Te_3, SiGe and PbTe based alloys and ZT values around one were achieved.[5] For several decades after, the search for good thermoelectric materials stopped and the only work in the field was at the system level. In 1990s, there was a renewed interest in thermoelectric modules initiated by the government, but this time from material perspective. The field restarted by looking into two distinct directions: first developing low dimensional materials and second developing new and perhaps more complex materials. [6]

Low dimensional materials have been the subject of intense study over the past couple of decades. Many review articles have been published which are focused on different classes of low dimensional materials such as superlattice structures and quantum wells, nanowires, and quantum dots. [7]–[12] Among low dimensional materials, one of the latest groups are 2D materials. The aim of this short review is to look at the latest advances in such materials relevant to thermoelectric field. We focus on monolayer and few layer structures and summarize both in-plane and cross-plane transport in these structures. We limit the in-plane discussion to only one example and that is graphene monolayers and bilayers. Graphene is by far the most studied 2D material. While it is not the best thermoelectric material, as we will explain later, it could be a very good choice for electronic cooling applications (the third mode of operation discussed above). In the cross-plane direction we focus on transport across few layers of 2D sheets also called layered van der Waals heterostructures. Since transport in these structures is ballistic (no scattering due to small thickness), it is more appropriate to refer to it as thermionic transport as opposed to cross-plane thermoelectric transport. Thermionic transport refers to transmission of hot electrons above an energy barrier. The 2D layered structures focused here are sandwiched between two metallic cathode and anode. Hot electrons inside the cathode have to pass above the energy barrier formed by the presence of the layered structure. The transmission properties in this case are not only a function of the layered structure but also the cathode and the anode layers and the interfaces formed between the materials. We summarize theoretical work as well as limited experimental results reported for such structures.

2. Advantage of 2D materials

In 1991 Hicks and Dresselhaus proposed that low dimensional materials are advantages for thermoelectric applications. The idea is to use sharp features in the density of states which are present in 2D (thin films), 1D (wires) and 0D (quantum dots) structures due to quantum confinement, to enhance the Seebeck coefficient. While there are debates in the literature regarding practicality and effectiveness of using quantum confinement effects to enhance the overall figure of merit [7], [13], the idea of using sharp features in the density of states to increase the Seebeck coefficient, remains valid. We can explain the idea conceptually as follows. Assume there is a temperature different along the sample.

Then the Fermi Dirac distribution function is broader at the hot side, which means there are more hot electrons (electrons above the chemical potential) at the hot side and more cold electrons (the ones below the chemical potential) at the cold side. As a result, hot electrons diffuse from hot to cold and cold electrons diffuse from cold to hot. If there are the same number of hot and cold electrons, then there will be a net zero voltage. However, if there is an imbalance between the number hot electrons and cold electrons, then a voltage is built up, which is the Seebeck voltage. One way of creating such an imbalance is to have asymmetry in the density of states (DOS) around the Fermi-level. In bulk materials, such asymmetry could be achieved by using a semiconductor and by setting the chemical potential to be close to the band minimum. The presence of the bandgap forbids cold electrons with energies smaller than the band minimum to exist and therefore creates an asymmetry between the number of hot and cold electrons. Other possible ways to have asymmetry between hot and cold electrons include but are not limited to semimetals with large asymmetry between conduction and valence effective masses[14], resonant doping [15] and use of materials with sharp f orbitals[16]. At low dimensions, density of states has intrinsic discontinuities which is the result of quantum confinement. Therefore, one can in principle tune the chemical potential close to the discontinuity energies to enhance the Seebeck coefficient.

Another benefit of low dimensional materials is their low thermal conductivity which is the result of the presence of many interfaces and short length scales that prevents phonons to effectively transport heat. However, this is not the case for 2D materials. In the in-plane direction of monolayer or few layer materials that are the focus of this paper, the thermal conductivity could be extremely large and it depends on the type of bonding between the atoms, the number density of the defects, and the coupling to the substrate. Graphene for example, has the record high thermal conductivity among all materials. Once placed on a substrate, its thermal conductivity drops significantly but still could be as high as 600 W/mK. In the cross-plane direction (i.e. across few layers) the thermal conductivity could be extremely small and it depends on the transmission and the coupling between the layers. In many of these structures, the layers are weakly bonded via van der Waals interactions and therefore thermal conductance could be very small. Therefore, in the cross-plane direction, usually layered materials are good for thermoelectric or thermionic applications while in the in-plane direction they are more optimistic for active cooling applications such as electronic cooling.

Another advantage of 2D materials is the possibility to tune their band gap. This could be achieved by changing the number of layers, applying strain or electric field and changing the structural composition of the material (by hydrogenation or oxidation). For example, arsenic is a typical group V semimetal in its bulk form. A puckered monolayer honeycomb structures of arsenic, called arsenene, is a semiconductor with indirect band gap of 0.831 eV [17]. Varying the number of layers, one can observe a smooth transition from semi-metallic to semiconducting state. It was shown that arsenene can be a direct gap semiconductor, a metal or a semimetal with Dirac cone similar to graphene depending on the strength and direction of applied strain [17]. Experimentally, strain could be applied by growing 2D materials on substrates that are having lattice mismatch with the deposited 2D-material. Applying a perpendicular electric field to a buckled honeycomb structure, another 2D form of arsenic, is shown to reduce and eventually close the band gap around 6 V/nm. In the next section of this article, we will summarize some of the latest advances in a handful classes of 2D materials.

3. Thermoelectric properties reported

a. Graphene

Experimental isolation of graphene [18], a single layer of carbon atoms arranged in a hexagonal honeycomb lattice, triggered an avalanche of studies devoted to 2D materials. In graphene, each carbon atom is $\mathbf{sp^2}$-hybridized and connected to three equidistant nearest neighbors by strong covalent σ-bonds oriented in-plane. The remaining unassociated $\mathbf{p_z}$-orbital electron sticks out of the plane and forms weak $\boldsymbol{\pi}$-bonds with neighboring orbitals of the same type. As a result, the highly-mobile delocalized $\boldsymbol{\pi}$-electrons are able to freely travel above and below a graphene sheet similar to a 2D electron gas. Intrinsic graphene is a zero band-gap semiconductor with a linear energy dispersion for both electrons and holes in the conduction and valence bands respectively. The conduction and valence bands touch each other at two inequivalent high-symmetry points (Dirac points) at the Brillouin zone edges, **K** and **K’,** forming Dirac cones. The dynamics of both electrons and holes are described by the relativistic Dirac equation for massless fermions rather than by the non-relativistic Schrodinger equation. The intrinsic electron and hole densities, $\boldsymbol{n}$ and $\boldsymbol{p}$, can be evaluated as follows $\boldsymbol{n = p = \frac{\pi}{6}\left(\frac{k_B T}{\hbar v_F}\right)^2}$, where $\boldsymbol{v_F \sim 10^8\ cm/s}$ is the Fermi velocity of carriers in graphene [19]. Thus, intrinsic carrier concentrations vary linearly from $\mathbf{10^8}\boldsymbol{cm^{-2}}$ at 10 K to $\mathbf{10^{11}}\boldsymbol{cm^{-2}}$ at room temperature. If the extrinsic disorder is eliminated, graphene possesses giant intrinsic mobility values as high as $\mu = \mathbf{2 \times 10^5}\,\boldsymbol{\frac{cm^2}{Vs}}$ at room temperature [20].

Most of the transport measurements are performed on graphene samples deposited on a substrate rather than suspended graphene. This is due to the difficulties in fabrication process of suspended samples [21], [22]. To the best of our knowledge, only one attempt to measure the Seebeck coefficient of suspended graphene has been made so far and the reported value is as low as 9 μV/K at room temperature indicating that the position of the Fermi level is close to the charge neutrality point (CNP) [22]. No gate voltage or carrier concentration dependence has been measured in this experiment.

Transport properties of graphene are strongly influenced by the underlying substrate.

Figure 2 shows how the sheet resistance, the Seebeck coefficient and the power factor of single and multi-layer graphene films grown on SiO_2 and hBN substrates change as a function of applied gate voltage and number of layers. Gate voltage modulation is equivalent to the scanning of chemical potential, μ, or to the change of doping concentration.

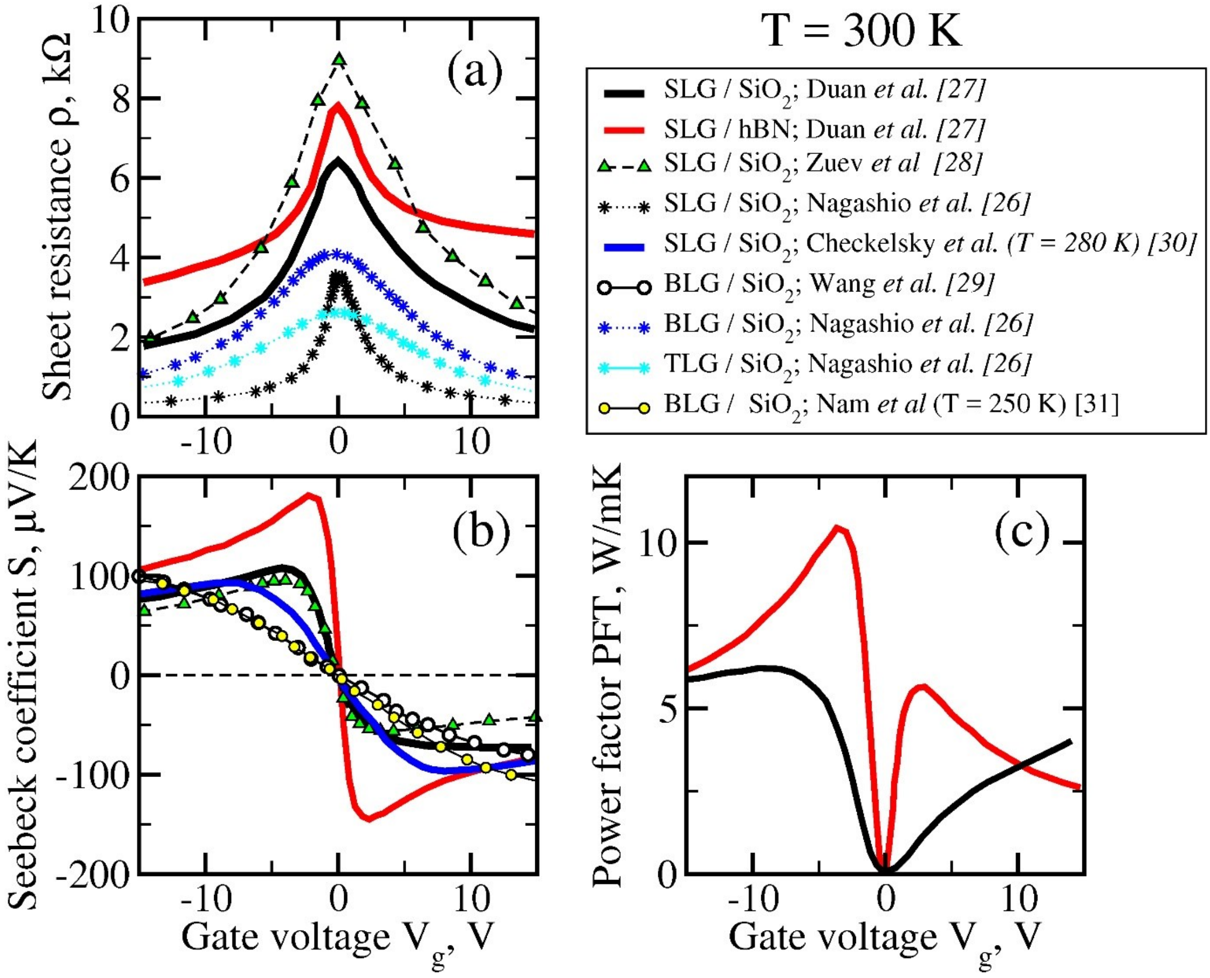


Figure 2. (a) Sheet resistance, (b) Seebeck coefficient and (c) thermoelectric power factor measured as a function of gate voltage for single layer graphene sheets grown on SiO_2 and hexagonal BN substrates as well as for bilayer and trilayer graphene on SiO_2 substrate at room temperature. We shift the charge neutrality point to zero voltage everywhere.

In intrinsic graphene, the resistivity maximum (conductance minimum) occurs at zero voltage, but in real systems, it is usually slightly shifted toward the point at which the average impurity potential is zero [23]. Here, we aligned all charge neutrality points at zero voltage for illustrative purpose. In theory, the resistance maximum of graphene at the Dirac point has a finite theoretical value, which is inversely proportional to the conductance quantum

$\boldsymbol{\sigma_{min}} = \frac{\boldsymbol{4e^2}}{\boldsymbol{\pi h}}$ [24]. This is a quantum mechanical effect and is a consequence of disorder which promotes a finite density of states at the Dirac point [24][25]. In actual experiments, the sheet resistance of graphene varies a great deal and depends strongly on the sample dimensions, sample quality, environmental conditions as well as on the underlying substrate. [26][27][28] Away from the Dirac point, the sheet conductance shows a linear and sublinear dependence with voltage [20].

SiO_2 is the most common substrate for graphene used nowadays. It has a number of drawbacks including roughness, high chemical reactivity and high content of charged impurities causing electron-hole charge fluctuations (or electron-hole “puddles”) in graphene [29]. On the contrary, graphene on an alkyl-terminated monolayer or hexagonal boron nitride (hBN) is chemically inert and avoids the problems mentioned above. As one can see in Figure 2, graphene on hBN (red solid curves) has a higher resistance which is misleading since in fact resistance depends on the geometry of graphene flake. When calculating conductivity, G/hBN owns larger conductivity and larger carrier mobility compared to G/SiO_2. It also has higher Seebeck coefficient than graphene (black solid [22], blue solid curves [30]) and bilayer (white [24] and yellow circles [31]) graphene on SiO_2. The combination of large mobility and large Seebeck coefficient results in a record high thermoelectric power factor, reported in G/hBN samples.

Graphene is an excellent thermal conductor with the largest known thermal conductivity. It outperforms other carbon-based materials including graphite, diamond and carbon nanotubes. The thermal conductivity of suspended graphene has been measured by different groups and a range of thermal conductivity values were reported which rely heavily on the assumptions used in these measurements. For example, at room temperatures, the reported values are in the range of 600 W/mK to few thousands W/mK. [32][33]–[35]. For in depth discussion of the differences between these measurements we refer the readers to a critical review by Li Shi[12]. Theoretical calculations help to reduce the uncertainty range to 2780-3600 W/mK and enable to understand mechanisms governing thermal transport in graphene. For instance, *ab initio* calculations predict $\boldsymbol{\kappa_L}$ = 3435 W/mK in Ref. [36], $\boldsymbol{\kappa_L}$ = 3260 W/mK in Ref. [37], $\boldsymbol{\kappa_L}$ = 3600 W/mK in Ref. [38] and molecular dynamics simulations with quantum corrections predict $\boldsymbol{\kappa_L}$ = 2782-2902 W/mK in Refs. [39], [40]. Interestingly, about 80% contribution to the thermal conductivity of graphene comes from the out-of-plane (flexural) ZA mode which has the quadratic dispersion [36], [37], [38], [39], [40] and heat is carried by collective excitations rather than single phonons as in 3D materials at room temperature [38], [40]. Bilayer graphene has intermediate thermal conductivity $\boldsymbol{\kappa_L} \approx$ 2200 W/mK between single layer graphene and graphite $\boldsymbol{\kappa_L} \approx$ 2000 W/mK [38]. The interaction with substrate significantly reduces the thermal conductivity due to the strong dissipative processes affecting the collective excitations [41].

Graphene is a semi-metal and, thus, has contributions from both phonons and charged carriers (“lattice” and “electronic” contributions respectively). Recent *ab initio* calculations revealed that the electronic contribution varies between 2 and 10% (~80-300 W/mK) of the total thermal conductivity and is higher at higher doping densities [42]. The Lorenz number $\boldsymbol{L(T)} = \frac{\kappa_e(T)}{\sigma(T)}\boldsymbol{T}$ obeys the Wiedemann-Franz law at low temperatures T < 200 K, where it is determined primarily by electron-impurity scattering, but deviates up to 50% at room temperature due to the dominant inelastic electron-phonon scattering [42]. The validity of Wiedemann-Franz law has been confirmed experimentally using a Joule self-heating method at low temperatures 50-160 K [43] and later at T < 150 K using Johnson noise thermometry experiments [44].

The electron mean-free paths in suspended graphene at room temperature are around 100 nm [42], while phonon mean free paths are much longer reaching up to 1 mm [38]. The thermal conductivity of graphene is strongly affected by the size of the sample [38], [45].

For example, the simulations show that 50% reduction of thermal conductivity can be achieved in the samples with L ≈ 2 μm [38]. The reduction of the thermal conductivity is explained by the increasing role of the phonon-boundary scattering when the size of the sample is smaller.

The high thermal conductivity of graphene makes it difficult to use it for thermoelectric applications. Several strategies to enhance the thermoelectric figure of merit in graphene, including defect engineering [46], band engineering [47] and nanostructuring [48], formation of isotopic superlattice structure ($^{12}C/^{13}C$)[49], reduction of thermal conductivity in oxidized graphene by using grain boundaries[50] and functionalization [51] are discussed in the literature. We believe, graphene is more suitable for active cooling applications. The combination of its large power factor and large thermal conductivity, makes it an ideal candidate for active cooling.[2], [27] It can primarily be used for electronic cooling applications in nano-electronics, where heat must be removed quickly to prevent overheating and, thus, damage to the device.

b. Two-dimensional layered materials

Two dimensional sheets of materials could be stacked to form weekly bonded layered structures. Each layer in two-dimensional layered materials (2DLMs) consists of a covalently bonded lattice and is weakly bound to neighboring layers by van der Waals interactions. This makes it feasible to isolate, mix and match dissimilar atomic layers to create a wide range of van der Waals heterostructures without the constraints of lattice matching and processing compatibility.[52] These structures have large anisotropy and the thermal conductivity in the cross plane direction tends to be low due to the van der Waals nature of the bonds. Therefore, such structures are good candidates for design of high ZT thermoelectric materials. Bismuth telluride, which has the record high ZT at room temperatures is a layered material itself with weekly bonded planes resulting in thermal conductivity values close to 1-2 W/mK at room temperatures. In this section, we will only focus on structures that are made with less than 3-10 monolayers sandwiched between metallic contacts and we only focus on cross-plane transport. We note that these structures are only on the order of 10 nm in thickness and electron and phonon transport is mostly ballistic. This implies that the device properties are not only a function the 2DLMs, but also a function of the metallic electrodes and the interfaces between the metal and the 2DLMs. We refer to these devices as thermionic devices.

Solid state thermionic power generators and refrigerators were first proposed by Shakouri [53] and Mahan [54] separately. These devices are made out of a semiconducting layer sandwiched between metallic electrodes. The semiconducting layer forms an energy barrier for electrons allowing only hot electrons to pass. This current flow is referred to as thermionic current. Vining and Mahan[55] used the B-factor to show that the efficiency of a thermionic device is almost always smaller than the efficiency of a thermoelectric device with similar parameters. However, they also noted that it is expected that the thermal conductance of a thermionic devices to be much smaller than its equivalent thermoelectric device due to size effects and Kapitza resistances at the interface. They identified that the biggest challenge for thermionic devices in terms of having efficiencies as high as thermoelectric devices and vacuum thermionic devices is to have extremely low thermal conductance values enabling establishment of large temperature drops at extremely small length scales. Zebarjadi [56] studied thermionic devices analytically and suggested that ideally thermal conductance values as low as 1 $\boldsymbol{MWm^{-2}K^{-1}}$ are needed for these structures.

2DLMs are perfect candidates for solid state thermionic devices due to their naturally low thermal conductance values as we pointed out before. Chen et al [57] studied thermoelectric transport in the cross plane direction of graphene/hBN/graphene structures. Despite their very low thermal conductance values, their reported ZT stayed as low as 10^{-6} due to small electrical conductance. hBN is insulating and forms too high of a barrier for electron transport. Li et al. [58] studied cross-plane transport of misfit layers of $(SnSe)_n(TiSe2)_n$. Again, the reported thermal conductivity was as low as 0.17 W/mK but the electronic transport was also very poor. This time not only due to low electrical conductivity but also due to relatively low Seebeck coefficient which could be attributed to positioning of n and p-type layers sequentially. Low thermal conductance values are also reported for other 2DLMs. Yuan et al. [59] reported values smaller than 1 $\boldsymbol{MWm^{-2}K^{-1}}$ for 7 layers of MoS_2 on c-Si. Massicotte et al.[60] studied photo-thermionic effect in graphene/WSe_2/graphene structures. They measured an extremely low thermal conductance values of 0.5 $\boldsymbol{MWm^{-2}K^{-1}}$ for 28nm thick WSe_2 sandwiched between graphene electrodes.

Perhaps one can purposely make rough contacts to lower the thermal conductance values or add imperfections and impurities at the contact. However, such strategies lower the electrical performance of these thermionic structures. It is critical to have clean Ohmic contacts between the metallic electrodes and the 2D layer structures to allow good electrical conductance. Therefore, only strategies such as acoustic mismatch or phonon dispersion mismatch at the contacts which are aimed at lowering of the thermal conductance without significantly modifying the electronic transport are optimistic.

Stacking 2D layers, forming clean interfaces for good electrical performance, and in situ connection of the 2D layers to metallic electrodes from top and back sides in vacuum to prevent oxidization at the 2D layer-metal contacts, are not easy tasks. Perhaps due to difficulties in making proper contacts, there has not been any report of observation of large equivalent figure of merit in 2DLMs sandwiched between metallic contacts. However, there are several theoretical studies that highlight the potential of 2DLMs in thermionic applications and predict large ZT values. Some of these theoretical predictions are summarized in Table 1. Wang et al. [61] studied thermionic transport across gold/graphene/black phosphorene/graphene/gold structures using first principles calculations. Consistent with experimental observations, they found that the bandgap of black phosphorene increases as the number of layers reduces from 5 layers to one layer. However, when the thickness is too small, the quantum tunneling current dominates, resulting in nonzero transmission in the energy gap. As a result of tunneling, the performance of monolayer phosphorene device was reported to be small. The performance increased when more layers were added to suppress the tunneling current. Later on, Wang et al. have studied Sc/WSe_2/n$MoSe_2$/WSe_2/Sc structure using first principles GW calculations and predicted ZT values above 3 at 600K, which is the result of proper band engineering and very low thermal conductance values. [62]

In contrast to Wang's work, Sadeghi et al. [63] obtained large cross-plane ZT values for monolayer of MoS_2 inserted between graphene electrodes. The difference is the use of MoS_2 ribbons instead of an infinitely large plane of MoS_2 with periodic boundary conditions. In the case of a thin ribbon (3.8nm thick in Ref. [63]), it was shown that transport through edge stages dominates the tunneling transport resulting in prediction of ZT values as large a three.

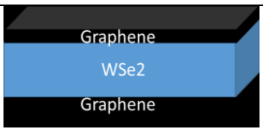
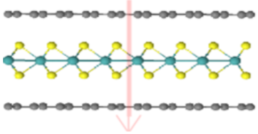
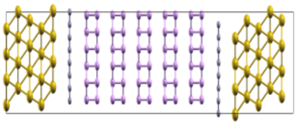
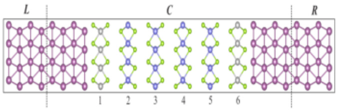
Device Schematic	Device Layers	Model	ZT	Ref
	Graphene (G)/62nm WSe$_2$/G	Phenomenological	>2	[64]
	G/MoS$_2$ /G	DFT- GGA	~3	[63]
	Gold/G/5-Black Phosphorous /G/Gold	DFT- HSE	0.13	[61]
	Scandium/WSe$_2$/4-MoSe$_2$ /WSe$_2$/Sc	DFT-GW	~3	[62]

Table 1. Theoretical predictions of the performance of 2D layer materials or Van der Waals heterostructures for thermionic applications.

4. Perspectives and Conclusions

2D materials are one of the latest classes of materials that are being investigated for thermoelectric applications. Many of these materials show very unique transport properties. Both in-plane and cross-plane thermoelectric properties are of interest. In this manuscript, we have limited ourselves to transport properties of graphene as a representative of in-plane thermoelectric transport, and to cross-plane thermionic transport in 2D layered materials.

Graphene is the most widely studied two-dimensional material possessing many unique physical properties. It demonstrates record high thermal conductivity and record high thermoelectric power factor. Therefore, it is ideal for active cooling applications wherein the goal is to cool down a hot spot fast and efficiently. The most relevant application is in electronic cooling to remove excess heat from computing chips. Despite many studies on graphene, there are still challenges in making a practical, robust cooler compatible with packaging and electronic industry. At the fundamental level, while the electrical conductance of graphene is well studied, the measurements of the Seebeck coefficient and evaluation of the full thermoelectric power factor are much scarcer. For example, there are no measurements of the Seebeck coefficient in suspended graphene as a function of doping concentration. There has not been any experimental study of thermoelectric transport properties of graphene at high temperatures. The effect of the substrate on thermoelectric properties of graphene is not fully understood. The quality of the samples as well as the quality of the substrate and the nature of the substrate, overwhelmingly affect the thermoelectric transport properties. Unpackaged samples are extremely sensitive to the environment, moisture and electric shock and are not practical to be used in electronics. Therefore, even in the case of graphene, there is a lot to be learned and explored.

There are also proposals to enhance the thermoelectric figure of merit of graphene by lowering its thermal conductivity. Proposed strategies include band engineering [47], defect engineering [46] and, most importantly, nanostructuring (*i.e.* making graphene nanoribbons) [48].

Finally, we discussed two-dimensional layered materials for thermionic applications. These materials are made out of dissimilar 2D atomic layers stacked on top of each other to form van der Waals heterostructure. In general, thermal conductivity of these materials is very low, while electrical transport in the out-of-plane direction is ballistic. Therefore, theoretically, they are promising candidates for solid state thermionic applications. There are several theoretical works at different levels of accuracy that all point out to the promise of 2DLMs for thermionic applications. However, there has not been any successful experimental demonstration of high performance solid state thermionic power generators. The biggest challenge is the fabrication of these small devices with proper metal contacts. Engineering of the interfaces to be clean and oxygen free for the purpose of good electronic transport with minimum thermal conductance is not an easy task. If successful, theoretical figure of merits as large as 3 are predicted for these structures.

Acknowledgements

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