

Thermal Transport in 2D Semiconductors—Considerations for Device Applications

Yunshan Zhao, Yongqing Cai, Lifa Zhang, Baowen Li, Gang Zhang,* and John T. L. Thong*

The discovery of graphene has stimulated the search for and investigations into other 2D materials because of the rich physics and unusual properties exhibited by many of these layered materials. Transition metal dichalcogenides (TMDs), black phosphorus, and SnSe among many others, have emerged to show highly tunable physical and chemical properties that can be exploited in a whole host of promising applications. Alongside the novel electronic and optical properties of such 2D semiconductors, their thermal transport properties have also attracted substantial attention. Here, a comprehensive review of the unique thermal transport properties of various emerging 2D semiconductors is provided, including TMDs, black- and blue-phosphorene among others, and the different mechanisms underlying their thermal conductivity characteristics. The focus is placed on the phonon-related phenomena and issues encountered in various applications based on 2D semiconductor materials and their heterostructures, including thermoelectric power generation and electron-phonon coupling effect in photoelectric and thermal transistor devices. A thorough understanding of phonon transport physics in 2D semiconductor materials to inform thermal management of next-generation nanoelectronic devices is comprehensively presented along with strategies for controlling heat energy transport and conversion.

Dr. Y. Zhao, Prof. J. T. L. Thong Department of Electrical and Computer Engineering National University of Singapore Singapore 117583, Republic of Singapore E-mail: john_thong@nus.edu.sg

Dr. Y. Cai, Dr. G. Zhang Institute of High Performance Computing, Singapore Singapore 138632, Republic of Singapore E-mail: zhangg@ihpc.a-star.edu.sg Prof. L. Zhang NNU-SULI Thermal Energy Research Center (NSTER) & Center for Quantum Transport and Thermal Energy Science (CQTES) School of Physics and Technology Nanjing Normal University Nanjing 210023, China Prof. B. Li Department of Mechanical Engineering University of Colorado Boulder, Colorado 80309, USA

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201903929.

DOI: 10.1002/adfm.201903929

1. Introduction

Since the first discovery of monolayer carbon atoms arranged in honeycomb structures,^[1,2] 2D graphene has inspired the community of materials scientists and opened up numerous competitive applications in electronics,^[3] spintronics,^[4] and valleytronics.^[5] Due to its strong in-plane covalent bonds formed by sp²-hybridized carbon arrangement, graphene exhibits many advantages compared with traditional materials, like super high electrical conductivity (high mobility of charge carriers)^[6] and superior thermal conductivity.^[7,8] As a zero bandgap semimetal,^[9,10] graphene is limited for field-effect-transistor (FET) applications since the carrier channel cannot be fully closed by gate voltage, resulting in a low working on/ off ratio (<10) that is typical for graphenechannel FETs.^[11] Following graphene, there is an increasing abundance of other members such as transition metal dichalcogenides (TMDs), black phosphorus (BP) etc. that have joined the 2D family, which also show excellent transport properties,

good mechanical flexibility and most importantly, interesting layer-tunable bandgaps. Recent high-field measurements of $MoS_2^{[12,13]}$ and black phosphorus^[14] show better performances than silicon in terms of both critical field and saturation velocity. Therefore, since discovery these kinds of 2D semiconductors are believed to be good candidates for post-silicon semiconductor technology^[15–17] due to their atomically thin channel and freedom from surface dangling bonds.

For 2D semiconductors with a honeycomb lattice that are noncentrosymmetric, such as TMDs, valley-contrasting electronic physics has led to the emergence of valleytronics, where the low-energy electronic states with handedness properties have been proven to create chiral optical excitations.^[18,19] Recently, it has been theoretically predicted^[20] and then experimentally observed^[21] that phonons in these materials (WSe₂) can have handedness or chirality as well. Chiral phonons are also observed in graphene/hexagonal boron nitride heterostructure,^[22] where chiral phonons are tunable and determine the selection rules of electronic intervalley scattering. This gives rise to potential applications in



valley tronics and phonon-chirality-based phononics.^[23] In quantum dots of WSe₂, the entanglement between chiral phonons and optical excitation have also been reported very recently.^[24]

Alongside the novel phononics and electronic/optical properties of 2D semiconductors, their thermal transport properties have drawn considerable interest as well. They are ideal platforms to study fundamental energy carrier transport and provide new directions for thermal energy control and management. As atomically thin layered structures held together by weak van der Waals forces, some 2D semiconducting materials show strong quantum confinement effect^[25,26] while the weak in-plane covalent bonds result in much lower thermal conductivity compared with that of graphene,^[7] which is beneficial for thermoelectric (TE) energy conversion purposes, where low thermal conductivity is needed to achieve high efficiency.^[27-29] On the other hand, with device scaling and increasing integration in modern integrated circuits, the power dissipation density has grown significantly, and hightemperature hot spots can lead to performance degradation as well as long-term reliability issues. Here a material with higher thermal conductivity alleviates the dissipation of the Joule heat originating from the active device, interconnects, and contacts. Typically, for heat conduction, Fourier's law is employed to characterize the heat conduction ability of a solid, and can be expressed as as $I = -\kappa \nabla T$, where I is the heat flux across the system, κ is the thermal conductivity, and ∇T is the temperature gradient. A better understanding of phonon transport in 2D semiconductors would aid in the design of novel devices that exploit such materials.

With increasing interest in new 2D materials, various fabrication methods have been proposed, namely top-down methods like mechanical/liquid exfoliation, and bottom-up methods like chemical vapor deposition (CVD) and wet-chemical synthesis.^[30-32] Generally exfoliated specimens are of better quality in terms of crystallinity that is consistent with their bulk counterparts while synthesis approaches yield the quantity needed for industrial applications.^[33,34] Regarding to the thermal properties of 2D materials, many research papers and review articles have been published. For theoretical calculation and simulation modeling, the reader can refer to refs. [35,36]. For thermal measurement methods, see refs. [37,38]. For a detailed survey of TE applications of 2D materials, readers can refer to refs. [39,40]. Our review takes a perspective from the various thermally related issues encountered in FETs based on 2D semiconductors, such as thermal management in the active device regions and interfacial thermal resistance across various contacts and interfaces. This article reviews phonon transport phenomena that are relevant not only to FET applications, but also to various other intriguing applications based on 2D semiconductor materials and their heterostructures. Specifically, we will include a discussion of several interesting works about functionalized 2D semiconductor materials for thermal transistor applications that have been reported recently. Our review aims to provide a thorough understanding of thermal transport issues in various applications based on 2D semiconductor materials, to pave the way for better thermal management and heat dissipation when designing next-generation nanoelectronic and energy conversion devices.



www.afm-journal.de



Yunshan Zhao is a Research Fellow in the Department of Electrical and Computer Engineering, National University of Singapore. He received his B.S. from Shandong University and Ph.D. from National University of Singapore. His current research mainly focuses on thermal/ thermoelectric transport in

low dimensional materials, such as nanowires and novel 2D materials.





Gang Zhang is a senior scientist and capability group manager at IHPC, Singapore. He received his B.S. and Ph.D. in physics from Tsinghua University in 1998/2002, respectively. His research is focused on the energy transfer and harvesting in nanostructured materials. He is a technical committee member for the International Electron Devices Meeting (IEDM).

John T. L. Thong obtained his B.A. (1985) and Ph.D. (1989) degrees from Cambridge University. He is currently a professor in the Electrical and Computer Engineering Department, National University of Singapore. His research interests are 1D and 2D materials, focusing on their electrical and thermal

properties with a particular reference to electronic device applications.

The outline of this review is as follows. A 2D semiconductorbased FET is shown in **Figure 1**, where various elements constituting the 2D semiconductor family are represented, like 1T- and 2H-MoS₂, BP, InSe, SnSe, and so on. Section 2 focuses on the unique thermal transport properties of these 2D semiconductors. As a representative TMDs, MoS_2 shows interesting thermal transport along the in-plane and out-of-plane directions, and the influence of layer-thickness and isotopes on its thermal transport will be discussed. Discussions on the anisotropic thermal transport behavior of BP and the ultralow thermal conductivity of SnSe for TE applications are included in this section. Electrical contacts to 2D semiconductor channels are typically made with





Figure 1. Representative 2D semiconductors that have been applied to FET devices. Various 2D semiconductors are shown, such as 1T- and 2H-MoS₂, BP, InSe, and SnSe.

metals and transport across such interfaces, including $MoS_2/$ contact and $MoS_2/substrate$ will be addressed in Section 3. In addition to these primary considerations in FET thermal management, thermal phenomena related to other device applications of 2D materials, i.e., thermoelectrics, electron–phonon coupling in photoelectric phenomena, effect of electrical field as well as strain on thermal property and thermal functional devices, like thermal transistor, are discussed in Section 4.

2. Thermal Properties in 2D Semiconductors

2.1. Transition Metal Dichalcogenides

Graphene is limited in its electronic device applications due to its lack of an electrical bandgap^[1] and this has prompted the search for similar 2D materials with semiconducting properties.



Transition metal dichalcogenides having the chemical formula of MX_2 , where M denotes a transition metal element and X represents a chalcogen element as shown in **Figure 2**, are promising candidates. With a reduction in the material thickness from bulk to monolayer, TMDs show an indirect- to directbandgap transformation, thus enabling potential applications for electronic and optoelectronic devices. While monolayer TMDs are semiconducting with bandgaps around 1–2 eV, the corresponding bulk TMDs show quite diverse properties from insulators and semiconductors to semimetals and true metals.^[31]

Because of the difference in lattice structure of TMDs compared with graphene, TMDs have different phonon transport behaviors, and show much lower thermal conductivity in theory and through experimental measurements. In contrast to dimension-dependence of thermal conductivity in graphene, thermal conductivity of TMDs typically shows near independence on size and roughness due to the very short intrinsic phonon mean free path (MFP).^[41] Moreover, compared to the strong sp2 C–C covalent bonds, the metal-chalcogen bond is much weaker due to its special sandwich structure, leading to variance in the phonon dispersions and Grüneisen parameters.^[41] All of these should be considered for thermal management in the design of nanoelectronic devices based on TMD materials.

Among the semiconducting TMDs, the thermal properties of Mo- and W-based materials are widely studied. Theoretically, the transition metal atom has a minimal effect on thermal conductivity for Mo- and W-based TMDs in the 2H structure and the thermal conductivity is mainly dominated by the chalcogen species, especially for the tellurides and selenides.^[42] From highfield electrical measurement and electrothermal modeling, the thermal conductivity of semi-metallic WTe₂ is 3 W m^{-1} $K^{-1[43]}$ while density functional theory (DFT) calculation yields a higher value of around 19 W $\mathrm{m}^{-1}~\mathrm{K}^{-1}$ for MoTe_2 and $\mathrm{WTe}_2.$ The thermal conductivity of single-layer and bilayer MoSe2 is 59 ± 18 and 42 ± 13 W m^{-1} K^{-1}, respectively, measured by optothermal Raman technique,^[44] which is comparable to the value calculated by classical nonequilibrium molecular dynamics (NEMD) simulations.^[45] While WS₂ shows a much larger thermal conductivity estimated from first-principles calculations than other S-based TMDs, due to a relatively large atomic weight difference induced phonon bandgap and suppressed

н		_		MX ₂													He
Li	Be			M = Ir X = Ch	ansition	n metal n						в	С	N	0	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	AI	Si	Ρ	s	CI	Ar
к	Ca	Sc	ті	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	i.	Xe
Cs	Ba	La - Lu	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	ті	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuo

Figure 2. Transition metals and chalcogen elements forming TMDs are highlighted in the periodic table. Reproduced with permission.^[31] Copyright 2013, Nature Research.



possibility of phonon–phonon scattering. This results in long phonon relaxation time. $^{\rm [46]}$

As one of the most stable TMDs, MoS₂ has been experimentally fabricated by various approaches, and thermal transport in this material has been widely explored. Nevertheless, the thermal conductivity values reported by different research groups diverge greatly. From ballistic NEGF calculations, the thermal conductivity of MoS2 nanoribbons has been shown to have a strong dependence on their orientation due to the different edge effect, and reported to be 673.6 and 841.1 W m^{-1} K⁻¹ for armchair and zigzag directions, respectively.^[47] Later on, first-principles-based Peierls-Boltzmann transport equation (PBTE) method predicted much lower thermal conductivity^[48] that is comparable to the experimental values. To further minimize the thermal conductivity, Ding et al. proposed MoS₂-MoSe₂ lateral superlattice structure,^[49] which showed close to 80% reduction in thermal conductivity compared with that of individual single-layer due to the enhanced anharmonic phonon scattering. On the other hand, even though it was theoretically predicted that the number of layers leads to different thermal conductivity as a result of the change in phonon dispersion and phonon scattering anharmonicity, the experimental data show much weaker layer dependence (Figure 3). The thermal conductivity is 34.5 ± 4 ,^[50] 77 ± 25 ,^[44] and 52 W $m^{-1}~K^{-1,[51]}$ for 1-layer (1-L), 2L, and 11L $MoS_2\!,$ measured by noncontact Raman spectrometry, where temperaturesensitive Raman peaks are commonly employed to deduce the thermal conductivity of 2D layered materials. Both thermal bridge method^[52] and e-beam technique^[53] give similar thermal conductivity values for 4L MoS₂, which are much smaller than that of bulk MoS₂ obtained by time-domain thermoreflectance (TDTR) technique.^[54] These experimental discrepancies are primarily attributed to the sample quality, such as extra PMMA induced surface disorders, as well as experimental measurement inaccuracies, which inevitably obfuscate the intrinsic thermal conductivity of MoS₂. For detailed descriptions of the measurement setups, the reader may refer to other review papers.[37,38]

Isotopic defects could affect the phonon transport by increasing phonon scattering.^[55,56] More recently, the isotope effect on thermal transport in monolayer MoS_2 has been



Figure 3. Thermal conductivity of MoS_2 as a function of layers numbers at room temperature. The κ is measured by various experimental techniques, including Raman spectrometer,^[44,50,51,59] thermal bridge method,^[52] e-beam heating technique,^[53] time-domain thermoreflectance (TDTR),^[54] and theoretical calculation by PBTE.^[48]

investigated,^[57] where the thermal conductivity of isotopically pure Mo ¹⁰⁰MoS₂ and 50% ¹⁰⁰MoS₂ was found to be higher by 50% and 30%, respectively, compared to that of natural MoS₂ comprising naturally abundant isotopes of Mo of various atomic masses of 92, 94, 95, 96, 97, 98, and 100.^[57,58] Due to the reduction of the isotopic disorder, the isotopically pure MoS₂ shows less isotope-phonon scattering, which enhances the phonon MFPs and thus the final thermal conductivity. These results are shown in **Figure 4**.

For other members having semiconducting property, like group IVB and VIII transition metal based TMDs, a much lower thermal conductivity has been theoretically shown, which is beneficial for TE applications.^[60] Typically, the thermal conductivity of the TMDs from these groups has a similar dependence on the chalcogen atom species and increases from selenides to sulfides. The thermal conductivity of monolayer ZrSe₂ and HfSe₂ at room temperature is 1.2 and 1.8 W m⁻¹ K⁻¹,^[61] respectively, which is lower than that of monolayer ZrS₂, of around



Figure 4. a) A sketch of different Mo isotoped-MoS₂. b) The sample length-dependent thermal conductivity of natural-MoS₂, ⁹²MoS₂, ⁹⁶MoS₂, and ¹⁰⁰MoS₂. Reproduced with permission.^[57] Copyright 2019, American Chemical Society.

FUNCTIONAL MATERIALS

3.2 W m⁻¹ K^{-1,[62]} Similarly, the thermal conductivity of monolayer $PdS_2^{[63]}$ is much larger than that of monolayer $PdSe_2$.^[64] It may be noticed that all these values are from theoretical calculations and more experimental work needs to be carried out to further explore the thermal transport behaviors of these TMDs.

More interestingly, unlikely the isotropic thermal transport in the in-plane direction of most TMDs, ReS_2 in a distorted 1T phase shows strong anisotropic thermal conductivity along and transverse Re-chains,^[65] which is similar to the thermal transport in puckered structures discussed below. Monolayer PdSe₂, due to its puckered morphology, shows direction-dependent thermal transport along its in-plane direction as well and the thermal conductivity of PdSe₂ along the *x*- and *y*-directions is 3.7 (1.4) and 7.2 (2.7) W m⁻¹ K⁻¹ at 300 K (800 K), respectively. This particular property could provide an additional degree of freedom in the design of nanoscale thermal devices based on these materials.

2.2. Phosphorene

Phosphorene, a single layer of phosphorus atoms arranged in a honeycomb-like structure, has drawn a great deal of attention as a promising 2D semiconductor due to its layer-tunable bandgap and high carrier (electron, hole) mobility, which is an important consideration for potential candidates for modern electronic applications, i.e., TE devices,^[66,67] photodetectors,^[68] and field-effect transistors.^[69,70] Phosphorene has two natural allotropes–blue phosphorene and black phosphorene,^[71,72] which show different lattice structures and thus have different phonon transport properties. Because of its special puckered honeycomb structure, black phosphorene exhibits interesting orientation-dependent phonon transport properties.^[73] As blue phosphorene is isotropic with a zigzag structure, phonon transport in this material does not depend on the orientation in the in-plane direction.^[71]

Typically, few-layer phosphorene is exfoliated from crystalline phosphorus by means of mechanical cleavage, and other techniques such as plasma-assisted process^[74] and liquidphase fabrication technique^[75] have been proposed as well. **Figure 5**a shows the atomic structure of black phosphorene, stacked together into black phosphorene by van der Waals force, and each atom is bonded to three neighboring atoms in sp^[3] hybridization configuration.^[76] Theoretically, it was predicted that phonon transport along zigzag (ZZ) direction is preferred compared to armchair (AC) direction and many first principles calculations have investigated this interesting anisotropic thermal transport,^[71,77–79] which is attributed to structural-asymmetry-induced phonon group velocity and relaxation time. It was demonstrated as well that the strain would have an inconsistent effect on the thermal transport along these two



Figure 5. a) Atomic structure of multilayer black phosphorus with top view of monolayer phosphorene shown in the inset. Reproduced with permission.^[76] Copyright 2016, Wiley-VCH. b) A summary of thickness dependent thermal conductivity of black phosphorene with various dimensions, like black phosphorene thin films, nanosheets and NRs. c) Thickness dependent Young's modulus, including both theoretical calculations and experimental measurement. Reproduced with permission.^[91] Copyright 2018, Wiley-VCH. d) 3D sketch of b-As structures. e) Comparison of in-plane anisotropy ratio of various properties along the AC and ZZ directions of b-As and other 2D materials. b-As has shown the maximum anisotropy ratio in both electrical conductivity and mobility while comparable thermal conductivity with other materials. f) Temperature-dependent thermal conductivity of b-As nanoribbons with dimension ≈ 124 nm along the ZZ and AC directions. Reproduced with permission.^[93] Copyright 2018, Wiley-VCH.





directions. By using nonequilibrium Green's functions method combined with first principles calculation, Ong et al.^[80] showed that the ZZ-oriented thermal conductance is increased when a strain is applied along this direction and decreases when an AC-oriented strain is applied; while the thermal conductance in AC orientation is always reduced when a strain is applied to either ZZ- or AC-directions. This inconsistent phonon response to strain possibly explains the recent experimental observation that Raman sensitive peak A_g^1 , B_{2g} , and A_g^2 modes could have opposite responses for tensile strain ZZ- and AC-directions.[81] By using a polymeric low-k dielectric to stretch the substrate, a high tensile strain of more than 7% was achieved in ref. [81], which nonetheless is still short of the theoretical predication of the high strain limit for ZZ and AC directions of 27% and 30%,^[82] respectively. Interestingly, the in-plane modes, B_{2g} and A_{σ}^{2} , show a red/blue shift when a strain is introduced along the ZZ and AC directions, respectively, due to the special in-plane puckered structure of BP. Even though the out-of-plane mode, A_g¹, remains unchanged for ZZ direction strain, it shows red shifting for AC direction strain. This study of strained BP provides insight into strain engineering of BP for electronic and optical devices.^[83,84]

Experimentally, different measurement techniques have been employed to explore the thermal transport anisotropy behaviors in black phosphorene, such as the use of suspended-pad thermal bridge,^[85,86] TDTR^[87,88] and micro-Raman spectroscopy,^[89] and the measurement results and sample dimensions are summarized in **Table 1**, where the anisotropy ratio are compared for different techniques as well. According to Zhu et al.,^[90] the strong anisotropy of thermal transport in black phosphorene is attributed to both group velocity variations and relaxation time variations along different crystalline orientations. The role of phonon relaxation time for thermal transport anisotropy is doubtful since dominant direction-dependent phonon dispersion^[85] and similar intrinsic phonon scattering rate along ZZ and AC directions^[89] were demonstrated.

More recently, Zhao et al.^[91] decoupled the dominant role of phonon group velocity from phonon relaxation time by linking the anisotropic phonon group velocity to anisotropic sound velocity, as verified by measuring the Young's modulus of black phosphorene along both ZZ and AC directions using method of three-point bending. It turns out that the anisotropy ratio between κ_{ZZ} and κ_{AC} is comparable to that of the Young's modulus value along these two directions. Considering the fact that the speed of sound, v_s^2 is proportional to the Young's modulus E and that the phonon group velocity could be treated as the speed of sound in the low frequency regime, the anisotropic phonon dispersion relation therefore accounts for the anisotropy observed in thermal transport between ZZ and AC directions. Further change of anisotropy ratio of thermal conductivity between ZZ and AC directions can be realized by the introduction of "nonsquare" pores in a phononic crystal (PnC),^[92] where phonon group velocity along the direction of more porous areas would be degraded more severely. This adjustable anisotropic ratio of thermal transport is a unique property of 2D phosphorene that can be exploited in thermal management applications.

As a cousin of black phosphorene, black arsenic (b-As) has just been fabricated and shows interesting anisotropic transport behaviors in electrical and thermal properties.^[93,94] Its puckered atomic structure, shown in Figure 5d, is similar to that of black phosphorene. Among the materials with puckered lattice structures, such as black phosphorene and other puckered materials, b-As has the greatest anisotropy in both electrical conductance and carrier mobility as shown in Figure 5e. For b-As, the electrical transport is more favorable in the AC direction than that in ZZ direction while thermal conductance just behaves in the opposite trend, similar to that of black phosphorene, which thus enables the implementation of novel transverse TE devices.^[93] Nevertheless, unlike BP which easily oxidizes, b-As demonstrates good resistance to ambient degradation.^[94]

Table 1. Thermal conductivit	y of BP at room temperature.
------------------------------	------------------------------

Dimension	Method	κ[W m ⁻¹ ł	Anisotropy ratio	
		AC	ZZ	ZZ/AC
Monolayer ^[95]	First-principles calculations	4.59	15.33	3.34
Monolayer ^[71]	First-principles calculations	36	110	3.06
Monolayer ^[78]	First-principles calculations	27.8	48.9	1.76
Monolayer ^[96]	MD simulation	63.6	110.7	1.74
Monolayer ^[73]	MD simulation	33.0	152.7	4.63
Monolayer ^[77]	First-principles calculations	24.3	83.5	3.44
Film (13–48 nm) ^[86]	Suspended-pad microdevices	5.8–9.6	7.8–13.2	1.34–1.36
NRs (60–300 nm) ^[85]	Suspended-pad microdevices	5.4-15.5	11.7–27	1.74–2.17
Film (9–30 nm) ^[89]	Micro-Raman spectroscopy	12.4–22	18.2–45.1	1.5–2
Film (39–277 nm) ^[97]	Four-probe measurement	17.3–24.5	64.9	≈3
NRs (106–220 nm) ^[91]	E-beam technique	13.5–20.6	30.5-38.6	1.99–2.33
Film (138–552 nm) ^[87]	TDTR	26.4-33.9	63-86.4	2.39–2.55
Bulk ^[88]	TDTR	28 ± 5	83 ± 10	≈2.96
Bulk ^[90]	TR-MOKE	26–36	84–101	≈3



2.3. Other 2D Semiconductors

Other than the TMDs and BP discussed above, the elements in Groups III to VI have drawn a lot of interest as well for interesting 2D layered semiconducting materials. Among them, the compounds of indium selenide, such as InSe and InSe₂ and compounds of bismuth telluride, such as Bi₂Te₃, Bi₂Se₃, and Sb₂Te₃ are the representative ones in various applications in optoelectronic devices,^[98] high-mobility filed-effect transistors,^[99] phase-change memory,^[100] single-mode phonon laser.^[101] and TE.^[102] The thermal transport in these materials has been studied quite recently. From EMD calculation, Bi₂Te₃ exhibits bulk-like thermal conductivity value when its thickness is around 5 nm, and the thermal conductivity has a nonmonotonic dependence on its thickness due to the interplay between Umklapp scattering and boundary scattering.^[103] Later experimental work by suspended pads measurement shows that the thermal conductivity increases with the thickness,^[102] as shown in Figure 6a, where the phonon-boundary scattering is dominant in the phonon transport.

Different from Bi₂Te₃ that has shorter phonon MFPs, InSe has relatively larger MFPs. The multiple crystalline phases of few-layered In₂Se₃ sheets are stable under experimental conditions,^[104] which provides the possibility of conducting further experimental study on other physical properties. In 2016, Zhou et al. measured the thermal conductivity of singlecrystal In₂Se₃ sheets.^[105] In₂Se₃ powders were used in the CVD growth of 2D In₂Se₃ sheets, and H₂ was used as the carrier gas. Through the temperature dependence of the phonon modes, thermal conductivity was measured using micro-Raman spectroscopy method. In general, in-plane thermal conductivity of In₂Se₃ sheets suspended across holes increases with increasing layer thickness in the range from 5 to 35 nm. Specifically, in this range of thickness, in-plane thermal conductivity increases from ≈ 4 to ≈ 60 W m⁻¹ K⁻¹. This thickness dependence is similar to that observed in supported graphene, but opposite that in suspended graphene sheets^[106] as shown in Figure 6a. This suggests the dominant role of phonon-boundary scattering in the thermal transport process in In₂Se₃, instead of phononphonon anharmonic scattering.

Other layered semiconducting materials belonging to these families have been proposed for TE applications considering



www.afm-journal.de

their ultralow thermal conductivity, such as GeAs₂^[107] and SnSe.^[108] Since the dimensionless figure of merit ≈2.62 was experimentally reported.^[109] layered SnSe has been considered as an excellent candidate for commercial development. Natural SnSe has a layered orthorhombic crystal structure and its monolayer has a highly puckered structure, very similar to that of puckered BP.^[109-111] Zhang et al. proposed a phase-controlled method to synthesize SnSe nanosheets^[112] and a single-crystalline SnSe nanosheet with thickness of ≈1.0 nm and lateral size of ~300 nm was synthesized experimentally.^[113] Using density functional theory combined with Boltzmann transport theory, Wang et al. studied thermal and thermoelectric properties of single-layered SnSe.^[108] It was demonstrated that anharmonic phonon-phonon interaction is dominant in the phonon scattering process, because of the remarkable overlapping between low frequency optical branches with the acoustic branches, as a consequence of the heavy atomic masses, weak interatomic bonds and the low atomic coordination. At room temperature, in addition to the contributions of acoustic branches to thermal conductivity, the low frequency optical modes also have nontrivial contributions. Thus, due to an anomalously high Grüneisen value and high anharmonicity of chemical bonds, there is strong anharmonicity in phonon-phonon scattering process, which leads to a low thermal conductivity (3.0 W m⁻¹ K⁻¹ for ZZ direction and 2.6 W m⁻¹ K⁻¹ for AC direction) in monolayer SnSe according to first-principles calculations.^[114] This strong phonon anharmonicity is theoretically attributed to the longrange interaction driven by the resonant bonding.^[95,115–117] The thermal conductivity of bulk SnSe is smaller than that of monolayer SnSe possibly due to the smaller interlayer interactions induced smaller phonon group velocity, as shown in Figure 6b, which thus contributes to better TE property considering its ultralow thermal conductivity (experimentally measured $\approx 0.25-0.28$ W m⁻¹ K⁻¹ at 773 K).^[109] The strong phonon anharmonicity was later demonstrated by inelastic neutron scattering (INS) measurement,^[118] where a softer transverse acoustic (TA) and transverse optic (TO) mode along Γ -X direction was observed than that of Γ -Y direction and this accounts for its anisotropic thermal transport as well.^[110] Unlike the weak direction dependence in thermal conductivity of SnSe, anisotropic and low thermal conductivity was presented in GeAs₂, a semiconductor formed from group IV and V elements. At room



Figure 6. a) Thickness dependent thermal conductivities of $In_2Se_3^{[105]}$ and $Bi_2Te_3^{[102]}$ by experimental measurement. A weak dimension dependent for Bi_2Te_3 is shown. b) Temperature-dependent thermal conductivity of monolayer GeS, GeSe, SnS and SnSe, and bulk SnSe. Reproduced with permission.^[114] Copyright 2016, Royal Society of Chemistry.



FUNCTIONAL MATERIALS

www.afm-journal.de

temperature, thermal conductivity of 6.03 W m⁻¹ K⁻¹ is reported along *a*-axis, while a much lower value of 0.68 W m⁻¹ K⁻¹ along the *b*-axis.^[107]

Similar to the role of transition metal in thermal conductivity of TMDs, the thermal conductivity of InSe was calculated to be lower than that of GaSe due to the enhancement in acoustic phonon velocity and in the reduction of scattering between acoustic and optical phonons.^[119–121] Moreover GaS has an overall larger thermal conductivity considering its even higher acoustic phonon velocity and weaker coupling of optical phonon modes with acoustic phonons.

3. Interface Thermal Resistance in 2D Devices

3.1. Interface Thermal Resistance (ITR) between 2D Materials and Dielectric Contacts

The thermal conductance at interfaces is a critical consideration for heat management in the scaling down of modern nanoelectronics devices, at length scales that are comparable to the MFP of energy carriers. This interfacial thermal resistance, or thermal boundary resistance (Kapitzal resistance) was initially discovered for helium-solid system^[122] and two theoretical models were accordingly developed, which are the acoustic mismatch model (AMM) and the diffusive mismatch model (DMM),^[123] depending on whether the heat carriers (phonons) are specularly scattered (AMM) or randomly and elastically scattered (DMM) at the interface. Therefore, the interfacial thermal resistance could be influenced by many factors, such as the interface roughness, chemical bonding and the atomic defects.^[124,125] For a more detailed theoretical modeling of heat transfer across interfacial boundaries, readers can refer to the review papers.[126,127]

For 2D based semiconductor devices, thermal transport at interfaces normally dominates in energy dissipation as well as in thermal management and thus understanding and characterization of interface heat transfer is necessary. Interface conditions also dominate the functionalities of these nanoelectronic devices. For example, trapped-charge induced Coulomb potential at the interface between the MoS₂ channel and the dielectric substrate is the dominant cause for the low carrier mobility in MoS2 field-effect devices.^[128] Just from a fundamental study point of view, 2D materials and especially their heterostructures provide an ideal platform to study interfacial heat transport along the cross-plane direction as a function of quantum-well exfoliation-controlled thickness. This has given rise to numerous studies in the past few years and this section is mainly focused on this topic. Modern advanced fabrication techniques have also enabled the realization of in-plane heterostructures^[129,130] with atomically sharp interfaces. However, interfacial thermal resistance measurement of such small lateral interfaces is much more challenging compared to more popular interface measurements between different materials in the cross-plane direction.

Besides TDTR^[131] and different 3ω techniques,^[132] which are preferred for bulk interface measurement, noncontact Raman thermometry is an attractive technique to characterize atomic interface thermal transport, especially for 2D layered materials. The Raman-sensitive peaks of the measured sample would serve as a temperature thermometer while the incident heat source is from the heating by either electrical^[133] or optical^[134,135] means. A sketch of a Raman laser heating setup is shown in Figure 7a, where the interface thermal transport across monolayer MoS2 and SiO2/AlN substrate is measured.^[136] For MoS₂, the positions of E_{2g}^1 and A_{1g} show redshift with increasing temperature, which works as a temperature indicator, and its absorption power is obtained from the absorbed incident laser power of one free-standing monolayer MoS₂ by considering the substrate enhancement effect. Although MD simulations^[124] show that the interface thermal conductance of MoS₂ on Au substrate is as high as 135–221 MW m⁻² K⁻¹, the results obtained by the Raman technique are considerably lower–0.44 \pm 0.07 MW m⁻² K⁻¹ for MoS₂-Au,^[44] 1.94 MW m^{-2} K⁻¹ for MoS₂-SiO₂,^[59] 17.0 MW m^{-2} K⁻¹ for MoS_2 -h-BN,^[137] and 15 MW m⁻² K⁻¹ for MoS_2 -AlN.^[136] The variations in the measured interface thermal conductance probably originate from the different interface quality prepared by the wet transfer method.^[138] Higher values obtained are possibly due to the better interface quality in the absence of polymeric residues.^[139] Temperature also affects the interface thermal transport as shown in Figure 7b, where the thermal boundary conductance (TBC) of MoS_2 -SiO₂ exhibits a T^{0.65} dependence. This temperature dependent interface thermal conductance agrees well with that of MoS₂-graphene interfaces simulated by MD calculation,^[140] which is theoretically attributed to the higher temperature-induced strong scattering of inelastic phonons and the presence of excited phonons.

By changing the thickness of the channel and increasing the spacing between the sample and substrate, the interface thermal transport could be tuned significantly. Layer-dependent interface thermal conductance of MoS_2 with c-Si substrate was measured by means of micro-Raman spectroscopy, which increases monotonically with the number of layers.^[138] Typically, the interface spacing leads to a higher Raman intensity and disturbs the local interface thermal transport as well. With decreasing number of layers, the Raman intensity difference between measured and theoretical values increases, implying a higher interface spacing, on the assumption that there is no spacing for the thickest MoS₂ (75 layers) for the theoretical Raman intensity calculation, which is shown in Figure 7c. The interface spacing would impair the interatomic forces between MoS₂ and substrates. Therefore, due to the higher interfacial energy coupling, thicker MoS₂ usually shows a better interface contact and the interface thermal conductance increases from 0.974 to 68.6 MW $\mathrm{m}^{-2}~\mathrm{K}^{-1}$ with increasing number of MoS_2 layers.^[138] The thickness-dependence of interface thermal conductance is shown in Figure 7d. A similar trend of interface thermal conductance on thickness was shown between WSe₂ and SiO₂ in ref. [141]. The layer-controllable interface thermal conductance of 2D semiconductors is favorable for FET applications considering the improved heat dissipation to the substrates without degrading the channel electrical transport.

3.2. ITR between 2D Materials and Metal Contact

Electrical contacts to devices are usually made using metals. Thus the interfacial thermal resistance between metal and







Figure 7. a) Sketch of monolayer MoS_2 on substrate and Raman thermometry measurement setup. b) Temperature dependent thermal boundary conductance (TBC) across MoS_2 -SiO₂, which follows trend of T^{0.65}. The graphs are from paper. Reproduced with permission.^[136] Copyright 2017, American Chemical Society. c) Change of measured- and theoretical calculated- Raman peak intensity of A_{1g} mode for MoS_2 -samples. d) Layer-dependent interface thermal conductance of MoS_2 -c-Si deduced from Raman sensitive E_{2g}^1 and A_{1g} modes. Reproduced with permission.^[138] Copyright 2017, Elsevier.

2D materials plays a critical role in thermal management of future 2D devices. There are two types of interface geometry: side contact and edge contact. Side contact can be made by contacting the metal surface with the plane of 2D materials. However, large contact resistance, for both electron and phonon, usually exists at the interface which drastically restrains the device current.^[142] Mao et al. studied interfacial thermal resistance in the side contact configuration between MoS₂ and Sc (Ru) through chemical bonding, and that between MoS₂ and Au (Pd) via weak physical bonding.^[143] As expected, the physisorbed case with a weaker bonding results in a much larger interfacial thermal resistance than the chemisorbed case. Compared with graphene/metal chemisorbed system, the metal/ MoS₂ chemisorbed contact is significantly more resistive, with almost 10-times higher thermal resistance. Therefore, for MoS₂ devices with side contact to metal electrodes, the interfacial thermal resistance is an impediment to heat dissipation.

On the other hand, for edge contacts, strong overlapping of electronic orbitals between the 2D material and metal electrode in most cases can lead to a substantial reduction in electron tunnel barrier and a great increase in electrical transport, which has been experimentally reported for both graphene^[144] and MoS₂ devices.^[145] By using molecular dynamics simulations, Liu et al. studied the interfacial thermal transport across the monolayer MoS₂ and Au electrode, where an edge contact was formed.^[124] The effect of surface orientation of the crystal gold electrode is also considered. As shown in **Figure 8**, although there is a remarkable dependence of interfacial thermal conductance on the interfacial structure, overall, the interfacial thermal conductance is large. For example, the largest value of interfacial thermal conductance occurs when $\theta = 0$ at the

(110) surface, about 2.21×10^8 W m⁻² K⁻¹. This is comparable to many commonly studied contact in semiconductor devices, for example, the Si/Ge (3×10^8 W m⁻² K⁻¹),^[146] Au–Si (1.88×10^8 W m⁻² K⁻¹),^[147] Al–Si (4.5×10^8 W m⁻² K⁻¹),^[148] and Cu–Si (4×10^8 W m⁻² K⁻¹),^[149] interfaces. It is worth emphasizing that although the thermal conductivity of graphene is nearly two orders higher than that of monolayer MoS₂, the contact thermal conductance of monolayer MoS₂ with metal contact is comparable to that of metal–graphene interfaces with a chemically bonded structure (2.5×10^8 W m⁻² K⁻¹),^[150] Thus edge contact between MoS₂ and metal electrodes has advantages in thermal management, in addition to the larger electrical current, compared to the side contact configuration.

In addition, the interfacial thermal conductance also depends on the interface configuration. At the MoS₂/Au (001) contact, the interfacial thermal conductance is robust and weakly dependent of the orientation angle. On the other side, for both MoS₂/Au (111) and MoS₂/Au (110) contacts, the interfacial thermal conductance decreases markedly when θ increases from 0° to 30°. For all the considered contacts, the interfacial thermal conductance decreases with the number of S vacancies, following a linear dependence.

4. Phonon-Driven Emerging Applications of 2D Semiconductors

4.1. Thermoelectric

The thermoelectric effect describes the conversion between heat and electrical energy.^[29,151,152] Heat is directly converted





Figure 8. a-c) MoS₂ on (001), (110), and (111) Au surfaces, respectively. Mo and S atoms are shown in purple and yellow color, and Au atoms in the first, second, and third layers are shown in cyan, brown, and red color, respectively. d) Interfacial thermal conductance on Au crystal surfaces with different contacting cases. Reproduced with permission.^[124] Copyright 2016, Springer.

into electricity through the Seebeck effect, and an electric current flow would lead to heat absorption and release, which is known as Peltier effect.^[153] The reversible generation of heat flow when an electric current passes through a conductor with a temperature gradient is called the Thomson effect.^[154] The efficiency of TE devices is normally characterized by a dimensionless figure of merit $ZT = (S^2T)/(\rho\kappa)$, where *S* is the Seebeck coefficient, *T* is the temperature, ρ is the electrical resistivity, and κ is the thermal conductivity, including both electron (κ_e)

contributions and phonon (κ_{I}) contributions. Thus, a higher ZT factor follows from a low thermal conductivity to generate a large temperature gradient, and high electrical conductivity to conduct electricity efficiently-desirable TE materials are those that behave like a phonon-glass electron-crystal.^[29,155] Typically, optimizing the material parameters is an exercise in compromise since they are correlated to each other. For example, the electrical conductivity of a material increases with increasing carrier concentration while the Seebeck coefficient decreases as it is physically related to the average entropy per charge carrier. Meanwhile, the carrier concentration induces a larger electrical thermal conductivity as related by the Wiedemann-Franz law.^[156,157] Therefore, good TE materials are typically degenerate semiconductors, as shown in Figure 9. According to Hicks and Dresselhaus,^[25,158] low dimensional nanostructures perform favorably for TE applications due to quantum confinement. Considering the staircase-like energy dependent density of states (DOS) of 2D materials shown in Figure 9b, 2D materials show better TE properties than those of bulk ones.

www.afm-journal.de

By electrolyte gating method, Pu et al. measured carrier densitydependent TE properties of monolayer MoS₂ and WSe₂.^[159] In this work, the authors fabricated the electric double-layer transistors based on centimeter-scale MoS₂, MoSe₂, and WSe₂ monolayers. In electric double-layer transistors, the dielectric layers of transistors are replaced with electrolytes. Therefore, it is possible to continuously increase the carrier density up to $5 \times 10^{13} \text{ cm}^{-2}$ and realize precise control of the Fermi level and Seebeck coefficient, owing to the high specific capacitance of electric double-layer. As shown in Figure 10, the absolute value of Seebeck coefficient of the monolayer samples is comparable with that of the bulk samples. However, at a similar Seebeck coefficient, the electrical conductivity of the 2D monolayers is a few orders of magnitude higher than that of the bulk samples. It turns out that the power factor of monolayer MoS₂ and WSe₂ is nearly one order of magnitude higher than that of their bulk materials counterparts, which provides direct evidence for the advantage of 2D monolayer sheets in thermoelectric application. Figure 10a,b compares the Seebeck coefficient and power factor of monolayers and their 3D bulk counterparts.

Given the combination of field-effect doping that can be well controlled, atomically clean surfaces, and quantum-well thickness variation, 2D semiconductors provide a versatile platform



Figure 9. a) Figure of merit as a function of reduced Fermi level $\eta^{[151]}$ and η is defined as $\eta = (E_F - E_0)/k_BT$, where E_F is the Fermi energy, k_B is the Boltzmann constant, and *T* is temperature. b) DOS, g(E), for bulk materials (3D), quantum well (2D), and quantum wire (1D). 2D is favorable for high power factor due to its staggered DOS. Reproduced with permission.^[151] Copyright 2010, Elsevier.







Figure 10. Comparison of electrical conductivity-dependent Seebeck coefficient a) and power factor b) for various TMDs, including bulk and monolayer MoS₂, MoSe₂, MoSe₂, MoTe₂, WS₂, and WSe₂. Reproduced with permission.^[159] Copyright 2016, American Physical Society.

to study the TE effect. MoS₂, as a representative 2D semiconductor, has shown attractive thermal as well as thermoelectric properties. Numerous theoretical papers^[160,161] have predicted its superior TE properties while spin-dependent thermal transport has been studied for sandwiched S-Mo-Se structure (Janus SMoSe).^[162] Earlier TE measurements focused on its photo-thermoelectric effect^[163] and the measured Seebeck coefficient value of single layer MoS₂ was between -4×10^2 to $-1 \times 10^5 \,\mu\text{V K}^{-1}$. Wu et al.^[164] later measured the Seebeck coefficient of monolayer CVD grown MoS₂ with values ≈ 30 mV K⁻¹, even though the conductivity was low and the authors demonstrated that the transport was dominated by variable-range hopping (VRH). Kayyalha et al.^[165] reported the thermoelectric transport properties of MoS2 with different number of lavers and it was shown that both electrical conductivity and Seebeck coefficient demonstrate a strong dependence on thickness (Figure 11a,b). With reducing thickness, the thermoelectric power factor (PF) keeps increasing until a peak, where a high $\approx 50 \ \mu\text{W} \text{ cm}^{-1} \text{ K}^{-2} \text{ PF}$ was shown for two-layer MoS₂ sample in its ON state, before dropping greatly for the monolayer, which was theoretically attributed to a difference in the energy dependence of the electron MFP. A similar thicknessdependent PF trend was reported in paper,^[166] where a relatively higher PF of two-layer MoS₂ was demonstrated due to the better conductivity in the degenerate metallic regime and a large Seebeck coefficient due to the high valley degeneracies and large effective masses. Quite recently, Wu et al.[167] showed that the PF of layered MoS₂ can be even enhanced by a strong interaction of electrons at the Fermi level with a local magnetic impurity (i.e., sulfur vacancy) and this socalled magnetic impurity-induced Kondo effect leads to a new record PF around 50 mW $m^{-1}\ K^{-2},$ as shown in Figure 11d. The single-atom sulfur vacancy in naturally grown MoS₂, confirmed by low-temperature scanning tunneling microscopy (STM) induces magnetic states, which further leads to a significant band splitting of $\approx 50 \pm 5$ meV at the conduction subband adjacent to the sulfur vacancy. The Kondo effect induced by magnetic impurities is seen to be an effective way to tune the Seebeck coefficient and ZT value for 2D semiconductor materials. Different from n-type MoS₂, WSe₂ shows interesting p-typed transport behavior. By means of gate-controlled surface carrier doping, Yoshida et al.^[168] showed that the optimization of power factor is possible in WSe₂ single crystals and the optimized values are comparable to those of a popular TE material, bismuth telluride, which is measured as 37 and 32 $\mu W \ cm^{-1} \ K^{-2}$ for p- and n- type conduction transport, respectively.

Like TMDs that have high mobility and tunable bandgap, layered black phosphorus has also been studied for its TE properties. As discussed in Section 2.2, BP exhibits unique anisotropic transport for both electrons and phonons, which is beneficial for TE performance, since the high electrical and thermal conductance directions are orthogonal to each other, enabling values of *ZT* above 1 for monolayer BP at a doping density of $\approx 2 \times 10^{20}$ cm⁻² along the AC orientation.^[169] Later experimental work was carried out on thicker material and it was found that Seebeck coefficient could reach up to +510 µV K⁻¹ in the hole depleted state at 210 K by using an EDIT configuration.^[66] Thickness-dependent thermoelectric characteristics of thick BP was studied as well,^[170] where Mott's VRH model was demonstrated to be the dominant mechanism in the TE and electrical transport of BP,^[170,171] as for the case of MoS₂.

Other 2D semiconducting materials, like n-type TiS₂^[172] and InSe^[173] have been recently explored as well for TE applications. As mentioned earlier, due to their weak interlayer van der Waals force, 2D layered semiconductors can be mechanically exfoliated into well-defined thickness down to single layer of a few angstroms thickness.^[174,175] By measuring thickness dependent TE properties in InSe, Zeng et al.^[176] have recently shown that the power factor increases greatly due to the sharper edge of the conduction-band DOS caused by quantum confinement and a Seebeck coefficient up to 570 µV K⁻¹ in 7 nm InSe sample has been reported. Further analysis shows that power factor in InSe would be increased significantly when the confined dimension is smaller than the thermal de Broglie wavelength, a scenario estimated by theoretical calculation.^[177] When the confined length increases beyond than the thermal de Broglie wavelength, the power factor decreases gradually toward the value for bulk InSe,^[178] which is shown in Figure 12.







Figure 11. a) Back-gate voltage (V_g - V_{th}) dependent thermoelectric power factor (PF) for different layers of MoS₂. b) PF versus the number of layers at different V_g - V_{th} . All the PF values are for room temperature. Reproduced with permission.^[165] Copyright 2016, American Institute of Physics. c) PF as a function of back-gate voltage. The bilayer MoS₂ shows a maximum PF with a larger electrical mobility. Reproduced with permission.^[166] Copyright 2017, American Physical Society. d) PF versus measured temperature for different back-gate voltages. An abnormal increase of PF is exhibited due to the Kondo effect. Reproduced with permission.^[167] Copyright 2019, arXiv.

4.2. Photoelectric (Electron-Phonon Coupling)

In addition to the direct effect to heat-to-electric energy conversion, phonons also play important roles in other energy conversion mechanisms, such as the photoelectric effect. Light-matter interaction is highly sensitive to the thermal environment of the material during the measurement. The coupling of the phonon and electron can renormalize the electronic structure, which can affect the light emission and absorption. Photocarriers, electrons and holes, can be scattered through a series of phonon coupling mechanisms satisfying the selection rules subject to energy and momentum conservation. In addition, thermal vibration distorts the ideal atomic positions and scatters the light-triggered electron-hole pairs. Specifically, acoustic phonons are involved in the carrier relaxation process via deformation potential interaction^[179] while optical/homopolar phonons are through Fröhlich interaction. For instance, TMDs such as MoS_2 and WS_2 show a strong absorption of visible light due to the "band nesting" effect. Photocarriers produced in the band-nesting part (located midway between the Γ and Λ points) drifts toward their immediate band extrema: Λ valley and Γ hill for electrons and holes, respectively.^[180] These electron-hole pairs are separated in the k-space and their radiative recombination requires either emission or absorption of single or multiple phonons. This indirect emission process results in low yield and the carrier lifetime

can be estimated to be 1 ns,^[181] which is in contrast to direct excitons with lifetime of around 100 ps and a higher quantum yield.^[182] Similarly, by using femtosecond time-resolved photoemission electron microscopy, the carrier dynamics property of monolayer WSe₂ on SiO₂/Si substrate has been studied to uncover the role of the intervalley electron–phonon scattering of electrons.^[183]

In monolayer or few-layer TMDs energy dissipation during nonradiative emission plays a vital role in the ultrafast processes of the carriers. Generally, two pathways of nonradiative energy channels exist after photoexcitation of layered TMDs^[184] (see **Figure 13**): 1) ultrafast cooling of hot carriers via electron– phonon scattering and subsequent formation of excitons, and 2) nonradiative recombination of excitons at the surface. While thermalization of the MoS₂ leads to a redshift of the exciton resonance energy due to electron–phonon scattering, the excess energy released from the cooling of hot carriers can be dissipated and transferred to the phonons within ≈2 ps for pathway 1), while process 2) is a Shockley–Read–Hall recombination responsible for energy dissipation from surfaces to external phonons within ≈9 ps.

In addition, phonons are also found to be important for the production of the excitons, a type of quasiparticle playing a significant role in the optical properties of layered semiconducting materials. The strength of the exciton-phonon can be obtained by experimentally measuring the dephasing





Figure 12. Power factor dependence on h_0/ξ at different carrier concentration.^[176] h_0 is the quantum confinement length and ξ the de Broglie wavelength. Power factor becomes saturated to bulk value when h_0/ξ is far large than 1. When the sample thickness is much smaller than the de Broglie wavelength, there is significant increase in thermal power due to quantum confinement. Reproduced with permission.^[176] Copyright 2018, American Chemical Society.

times,^[185] exciton linewidths and mobility,^[186] and photoluminescence,^[187] Different from excitons in bulk GaAs materials where the excitons are predominantly located at the center of the Brillouin zone thus carrying zero momentum, excitons in TMDs are formed at the noncentral points in the momentum space.^[188] This induces dramatic differences in the pathways of the exciton creation between GaAs and TMDs. For these nonzero wavevector excitons, the subsequent relaxation to the zero wavevector momentum involves emission of acoustic phonons or longitudinal optical (LO) phonons. A model within the framework of Fermi's Golden rule was established to derive the formation dynamics of excitons from free carriers in TMDs.^[189] Depending on the density of the electrons and holes, nonzero momentum excitons could be generated from free electron–hole pairs in layered materials via the longitudinal optical phonons coupling of charge carriers at high temperature (≈120 K). On the other hand, in monolayer TMDs, excitons can be relaxed by phonons by means of the deformation potential or in the process of piezoelectric coupling. This relaxation effect could be as important as those by defect-assisted scattering or trapping effect by the surface states.^[190] Photoluminescence study of monolayer MoS₂ highlighted the importance of exciton-phonon coupling.^[191]

In addition to phonon-phonon, phonon-boundary and phonon-defect scattering, the phonon lifetime can be modulated by other factors as well. In particular, due to their atomic thickness, the phonon properties of 2D materials are extremely sensitive to environment, including substrate, electrical field, etc. One example is for free-standing and supported graphene. As well known, there are three acoustic phonon modes in monolayer freestanding graphene, the in-plane longitudinal acoustic mode (LA), in-plane transverse acoustic mode and out-of-plane flexural mode (ZA), and at Brillouin zone center, the energy of these acoustic modes is zero. However, for supported graphene, while the in-plane LA and TA modes are slightly influenced, the ZA mode is flattened and shifted. Obviously, a new flexural mode, called ZA' mode appears with energy of 6 THz at Γ point. This is because the substrate can break the translational invariance at the out-of-plane direction. The mismatch in flexural modes can induce significant resistance for heat flow through boundary between free-standing and supported graphene.^[192] Furthermore, due to the different lattice constant between the supported 2D materials and substrate, there exists strain (stress) in the 2D materials. Usually, tensile strain results in softening of the bonds, reducing the phonon group velocity and enhancing the phonon-phonon anharmonic scattering strength. The combination of all these factors will reduce the thermal conductivity of 2D materials.^[193] However, for thermal conductance of certain 2D materials, for example, borophene, tensile strain may increase its thermal conductance along certain crystal axis, because of



Figure 13. a) Schematic for visible (vis), near-infrared (NIR), and mid-infrared (MIR) detection irradiation in MoS₂. Possible optical transitions are marked by dashed and solid straight arrows caused by the pump pulse and probe pulse. b) Sketch of nonradiative energy channels that follow the ultrafast excitation. Reproduced with permission.^[184] Copyright 2018, American Chemical Society.



www.afm-journal.de

the change in the bond environment^[194] and for monolayer silicene, tensile strain would greatly increase its thermal conductivity due to the enhancement in the acoustic phonon lifetime.^[195]

Moreover, the interactions between electron and phonon would affect the thermal transport property of 2D materials as well. In electronic devices based on 2D materials an electric field always exists. For some polar materials, the electric field may have a direct influence on their phonon vibrational modes, consequently affecting the thermal conductivity. For nonpolar materials, electric field may provide indirect effect on thermal conductivity through electron-phonon coupling.^[196] Using fully first-principles calculations, Liao et al.[197] studied the effect of electron-phonon interaction on phonon transport, and compared this effect with the intrinsic phonon-phonon anharmonic interaction. Using silicon as an example, they found a significant reduction in the lattice thermal conductivity due to

electron–phonon interaction when the carrier density exceeded 10^{19} cm⁻³. It is worth mentioning that for p-type silicon with hole density of 10^{21} cm⁻³, electron–phonon coupling can induce 45% reduction in its room temperature thermal conductivity. Considering the fact that this is a typical range of carrier concentration in the electronic devices and thermoelectric devices, the electron–phonon coupling cannot be ignored in a study of thermal conductivity of semiconductors. The impact of electron–phonon interaction on thermal conduction of 2D materials deserves future studies.

4.3. Thermal Transistor Devices

Engineering the physical characteristics of phonons provides a powerful way to realize designable thermal functional materials. Furthermore, achieving active control of heat flow in a manner analogous to electronic circuits represents a game changer in engineering energy transport. Theoretical models to realize various types of thermal devices have been developed.^[198,199] Because of the advantages of high thermal conductivity, single-atom thickness and tunable shape, graphene-based thermal rectifier^[200–204] and thermal modulator^[205] have been explored both theoretically and experimentally.

Recently, Sood et al. demonstrated experimentally a thermal transistor based on MoS_2 thin film actuated by reversible electrochemical intercalation of Li ions.^[206] Conceptually, thermal transistor is a device whose thermal conductance can be modulated via an external stimulus, such as electrical voltage. For the MoS_2 based thermal transistor, the on-state corresponds to the pristine MoS_2 and the off-state corresponds to the Li-intercalated MoS_2 . **Figure 14**a shows the schematic of the device under operation. It is a 10 nm thick few-layer MoS_2 film, and $LiPF_6$ in ethylene carbonate/diethyl carbonate serves as the liquid electrolyte. Charging/discharging the cell is controlled by electrical current in a manner of real-time modulation. As shown in Figure 14b, during the lithiation step, the MoS_2 working electrode



Figure 14. a) Illustration of the thermal transistor under operation. b) The MoS₂ working electrode VWE measured during the electrochemical cycle. c) Cross-plane thermal conductance during the electrochemical cycle. Reproduced with permission.^[206] Copyright 2018, Nature Research.

decreases as Li ions enter the MoS_2 films. Consequently, the cross-plane thermal conductivity decreases from about 15 to 1.6 MW m⁻² K⁻¹ as shown in Figure 14c. When the current is reversed during the delithiation step, Li ions are removed from the MoS_2 film, and the cross-plane thermal conductance increases back to the pre-lithiation value. The on/off ratio is about 10 times between the lithiated and delithiated states.

The underlying mechanism was examined using first-principles calculations. The pre-lithiation MoS_2 film is in 2H phase with ABAB stacking sequence. Upon intercalation, Li ions occupy the octahedral sites inside the interlayer gap, forming 2H-Li₁MoS₂ phase and mixed with 1T-Li₁MoS₂ phase with stacking sequence AA. As shown in Figure 15a–c, lithiation



Figure 15. Phonon dispersions along the cross-plane direction. a) 2H-MoS₂, b) 1T-Li₁MoS₂, and c) 2H-Li₁MoS₂. Blue curves show the contribution from MoS₂ and red curves show that from Li atoms. Reproduced with permission.^[206] Copyright 2018, Nature Research.





gives rise to several flat bands, results in decreased group velocity and increased phonon scattering rates according to phonon rattling effect,^[207] and consequently leads to a reduction in thermal conductivity. Moreover, lithiation may induce disordered stacking among MoS_2 film, lead to significant reduction in cross-plane thermal conductivity. Thus the observed thermal transistor is due to lithiation induced phonon scattering, reduction in group velocity and stacking disorder.

5. Conclusions and Outlook

In this article, various thermal issues related to 2D semiconductors in various electrical applications are discussed. With the rapid discovery of various 2D semiconductors, better understanding of their thermal transport properties is necessary for thermal management and energy conversion. We consider the effect of various conditions on phonon transport of channeling materials, such as strain, orientations and dimensions effect, etc. We have focused on the experimental thermal property measurement of 2D semiconductors obtained by various techniques, and the inconsistency with theoretical predication implies that new techniques with improved accuracy of measurement are needed as well as better device fabrication of 2D semiconductors. Furthermore the interfacial thermal resistance across channel/substrate and channel/contact has been discussed. Other than the direct influence on thermal management and dissipation, thermal properties related to the applications of 2D semiconductors have been discussed, including the TE effect, electron-phonon coupling effect in photoelectric phenomena, and thermal transistor devices.

Advanced fabrication techniques have made the preparation of various stable 2D materials with novel properties possible, and multistage circuit integration of 2D materials has been demonstrated recently, which is a crucial step toward 2D applications in the next-generation electronic devices. Together with the interesting electrical/optical/optoelectronic properties of novel 2D semiconductors, their thermal and thermoelectric properties should be considered as well, which is believed to be an immature field and needs more investigations. The energy dissipation at the interface should be re-considered as well when designing the nanoscale devices based on 2D materials given the large number of interfaces involved in an integrated circuit. From the fundamental study point of view, there are currently limited options to experimentally study thermal transport in 2D semiconductors and new complementary techniques should be developed to enable more systematic studies to understand their novel phonon transport behaviors.

Acknowledgements

The authors gratefully acknowledge funding from A*STAR SERC, Grant No. 1527000015.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D semiconductors, interface thermal resistance, phonon transport, thermal functional device

Received: May 16, 2019 Revised: August 2, 2019 Published online:

- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 2004, *306*, 666.
 A. K. Geim, K. S. Novoselov, *Nat. Mater.* 2007, 6, 183.
- [2] A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183.
- [3] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, J. Hone, *Nat. Nanotechnol.* 2010, *5*, 722.
- [4] W. Han, R. K. Kawakami, M. Gmitra, J. Fabian, Nat. Nanotechnol. 2014, 9, 794.
- [5] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, *81*, 109.
- [6] M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher Jr., T. F. Baumann, J. Am. Chem. Soc. 2010, 132, 14067.
- [7] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* **2008**, *8*, 902.
- [8] A. A. Balandin, *Nat. Mater.* **2011**, *10*, 569.
- [9] I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, K. L. Shepard, Nat. Nanotechnol. 2008, 3, 654.
- [10] F. Schwierz, Nat. Nanotechnol. 2010, 5, 487.
- [11] F. Schwierz, Proc. IEEE 2013, 101, 1567.
- [12] K. K. Smithe, C. D. English, S. V. Suryavanshi, E. Pop, Nano Lett. 2018, 18, 4516.
- [13] A. Serov, V. E. Dorgan, A. Behnam, C. D. English, Z. Li, S. Islam, E. Pop, Proc. SPIE 2014, 9083, 908307.
- [14] X. Chen, C. Chen, A. Levi, L. Houben, B. Deng, S. Yuan, C. Ma, K. Watanabe, T. Taniguchi, D. Naveh, X. Du, F. Xia, ACS Nano 2018, 12, 5003.
- [15] H. Liu, A. T. Neal, P. D. Ye, ACS Nano 2012, 6, 8563.
- [16] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, ACS Nano 2014, 8, 1102.
- [17] Z. Yu, Y. Pan, Y. Shen, Z. Wang, Z.-Y. Ong, T. Xu, R. Xin, L. Pan, B. Wang, L. Sun, J. Wang, G. Zhang, Y.-W. Zhang, Y. Shi, X. Wang, *Nat. Commun.* **2014**, *5*, 5290.
- [18] D. Xiao, G. B. Liu, W. Feng, X. Xu, W. Yao, Phys. Rev. Lett. 2012, 108, 196802.
- [19] K. F. Mak, K. He, J. Shan, T. F. Heinz, Nat. Nanotechnol. 2012, 7, 494.
- [20] L. Zhang, Q. Niu, Phys. Rev. Lett. 2015, 115, 115502.
- H. Zhu, J. Yi, M. Y. Li, J. Xiao, L. Zhang, C. W. Yang, R. A. Kaindl,
 L. J. Li, Y. Wang, X. Zhang, *Science* 2018, 359, 579.
- [22] M. Gao, W. Zhang, L. Zhang, Nano Lett. 2018, 18, 4424.
- [23] H. Chen, W. Zhang, Q. Niu, L. Zhang, 2D Mater. 2018, 6, 012002.
- [24] X. Chen, X. Lu, S. Dubey, Q. Yao, S. Liu, X. Wang, Q. Xiong, L. Zhang, A. Srivastava, Nat. Phys. 2019, 15, 221.
- [25] L. Hicks, T. Harman, X. Sun, M. Dresselhaus, *Phys. Rev. B* **1996**, *53*, R10493.
- [26] G. W. Mudd, S. A. Svatek, T. Ren, A. Patanè, O. Makarovsky, L. Eaves, P. H. Beton, Z. D. Kovalyuk, G. V. Lashkarev, Z. R. Kudrynskyi, A. I. Dmitriev, *Adv. Mater.* 2013, *25*, 5714.
- [27] J. P. Heremans, V. Jovovic, E. S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G. J. Snyder, *Science* **2008**, *321*, 554.
- [28] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J. P. Fleurial, P. Gogna, Adv. Mater. 2007, 19, 1043.
- [29] D. M. Rowe, CRC Handbook of Thermoelectrics, CRC Press, Boca Raton, FL 1995.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [30] G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano, V. R. Cooper, L. Liang, S. G. Louie, E. Ringe, W. Zhou, S. S. Kim, R. R. Naik, B. G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N. Alem, J. A. Schuller, R. E. Schaak, M. Terrones, J. A. Robinson, ACS Nano 2015, 9, 11509.
- [31] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, Nat. Chem. 2013, 5, 263.
- [32] R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, F. Zamora, Nanoscale 2011, 3, 20.
- [33] H. Zhang, ACS Nano 2015, 9, 9451.
- [34] J. Hong, Z. Hu, M. Probert, K. Li, D. Lv, X. Yang, L. Gu, N. Mao, Q. Feng, L. Xie, J. Zhang, D. Wu, Z. Zhang, C. Jin, W. Ji, X. Zhang, J. Yuan, Z. Zhang, *Nat. Commun.* **2015**, *6*, 6293.
- [35] G. Zhang, Y.-W. Zhang, Chin. Phys. B 2017, 26, 034401.
- [36] X. Gu, Y. Wei, X. Yin, B. Li, R. Yang, Rev. Mod. Phys. 2018, 90, 041002.
- [37] Y. Wang, N. Xu, D. Li, J. Zhu, Adv. Funct. Mater. 2017, 27, 1604134.
- [38] X. Xu, J. Chen, B. Li, J. Phys.: Condens. Matter 2016, 28, 483001.
- [39] J. Wu, Y. Chen, J. Wu, K. Hippalgaonkar, Adv. Electron. Mater. 2018, 4, 1800248.
- [40] Y. Zhou, L. D. Zhao, Adv. Mater. 2017, 29, 1702676.
- [41] X. Wei, Y. Wang, Y. Shen, G. Xie, H. Xiao, J. Zhong, G. Zhang, Appl. Phys. Lett. 2014, 105, 103902.
- [42] D. O. Lindroth, P. Erhart, Phys. Rev. B 2016, 94, 115205.
- [43] M. J. Mleczko, R. L. Xu, K. Okabe, H.-H. Kuo, I. R. Fisher, H.-S. P. Wong, Y. Nishi, E. Pop, ACS Nano 2016, 10, 7507.
- [44] X. Zhang, D. Sun, Y. Li, G.-H. Lee, X. Cui, D. Chenet, Y. You, T. F. Heinz, J. C. Hone, ACS Appl. Mater. Interfaces 2015, 7, 25923.
- [45] Y. Hong, J. Zhang, X. C. Zeng, J. Phys. Chem. C 2016, 120, 26067.
- [46] X. Gu, R. Yang, Appl. Phys. Lett. 2014, 105, 131903.
- [47] J.-W. Jiang, X. Zhuang, T. Rabczuk, Sci. Rep. 2013, 3, 2209.
- [48] X. Gu, B. Li, R. Yang, J. Appl. Phys. 2016, 119, 085106.
- [49] G. Ding, J. He, G. Gao, K. Yao, J. Appl. Phys. 2018, 124, 165101.
- [50] R. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A. R. Hight Walker, H. G. Xing, ACS Nano 2014, 8, 986.
- [51] S. Sahoo, A. P. Gaur, M. Ahmadi, M. J.-F. Guinel, R. S. Katiyar, J. Phys. Chem. C 2013, 117, 9042.
- [52] I. Jo, M. T. Pettes, E. Ou, W. Wu, L. Shi, Appl. Phys. Lett. 2014, 104, 201902.
- [53] A. Aiyiti, X. Bai, J. Wu, X. Xu, B. Li, Sci. Bull. 2018, 63, 452.
- [54] J. Liu, G.-M. Choi, D. G. Cahill, J. Appl. Phys. 2014, 116, 233107.
- [55] N. Yang, G. Zhang, B. Li, Nano Lett. 2008, 8, 276.
- [56] S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A. A. Balandin, R. S. Ruoff, *Nat. Mater.* **2012**, *11*, 203.
- [57] X. Li, J. Zhang, A. A. Puretzky, A. Yoshimura, X. Sang, Q. Cui, Y. Li, L. Liang, A. W. Ghosh, H. Zhao, R. R. Unocic, V. Meunier, C. M. Rouleau, B. G. Sumpter, D. B. Geohegan, K. Xiao, ACS Nano 2019, 13, 2481.
- [58] Q. Lu, A. Masuda, Int. J. Mass Spectrom/ Ion Processes 1994, 130, 65.
- [59] A. Taube, J. Judek, A. Łapińska, M. Zdrojek, ACS Appl. Mater. Interfaces 2015, 7, 5061.
- [60] D. Qin, X.-J. Ge, G. Ding, G. Gao, J.-T. Lü, RSC Adv. 2017, 7, 47243.
- [61] G. Ding, G. Gao, Z. Huang, W. Zhang, K. Yao, Nanotechnology 2016, 27, 375703.
- [62] H. Lv, W. Lu, D. Shao, H. Lu, Y. Sun, J. Mater. Chem. C 2016, 4, 4538.
- [63] Y.-S. Lan, Q. Lu, C.-E. Hu, X.-R. Chen, Q.-F. Chen, Appl. Phys. A 2019, 125, 33.
- [64] D. Qin, P. Yan, G. Ding, X. Ge, H. Song, G. Gao, Sci. Rep. 2018, 8, 2764.
- [65] H. Jang, C. R. Ryder, J. D. Wood, M. C. Hersam, D. G. Cahill, Adv. Mater. 2017, 29, 1700650.

- [67] E. Flores, J. R. Ares, A. Castellanos-Gomez, M. Barawi, I. J. Ferrer, C. Sánchez, Appl. Phys. Lett. 2015, 106, 022102.
- [68] M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. Van Der Zant, A. Castellanos-Gomez, *Nano Lett.* 2014, 14, 3347.
- [69] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, Nat. Nanotechnol. 2014, 9, 372.
- [70] S. P. Koenig, R. A. Doganov, H. Schmidt, A. Castro Neto, B. Oezyilmaz, *Appl. Phys. Lett.* **2014**, *104*, 103106.
- [71] A. Jain, A. J. McGaughey, Sci. Rep. 2015, 5, 8501.
- [72] Y. Aierken, D. Çakır, C. Sevik, F. M. Peeters, Phys. Rev. B 2015, 92, 081408.
- [73] W. Xu, L. Zhu, Y. Cai, G. Zhang, B. Li, J. Appl. Phys. 2015, 117, 214308.
- [74] W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jin, Z. Zhang, *Nano Res.* **2014**, *7*, 853.
- [75] P. Yasaei, B. Kumar, T. Foroozan, C. Wang, M. Asadi, D. Tuschel, J. E. Indacochea, R. F. Klie, A. Salehi-Khojin, *Adv. Mater.* 2015, *27*, 1887.
- [76] V. Eswaraiah, Q. Zeng, Y. Long, Z. Liu, Small 2016, 12, 3480.
- [77] L. Zhu, G. Zhang, B. Li, Phys. Rev. B 2014, 90, 214302.
- [78] T.-H. Liu, C.-C. Chang, Nanoscale 2015, 7, 10648.
- [79] G. Qin, M. Hu, Small 2018, 14, 1702465.
- [80] Z.-Y. Ong, Y. Cai, G. Zhang, Y.-W. Zhang, J. Phys. Chem. C 2014, 118, 25272.
- [81] W. Zhu, L. Liang, R. H. Roberts, J.-F. Lin, D. Akinwande, ACS Nano 2018, 12, 12512.
- [82] Q. Wei, X. Peng, Appl. Phys. Lett. 2014, 104, 251915.
- [83] Y. Wang, C. Cong, R. Fei, W. Yang, Y. Chen, B. Cao, L. Yang, T. Yu, *Nano Res.* 2015, *8*, 3944.
- [84] S. Zhang, N. Mao, J. Wu, L. Tong, J. Zhang, Z. Liu, Small 2017, 13, 1700466.
- [85] S. Lee, F. Yang, J. Suh, S. Yang, Y. Lee, G. Li, H. S. Choe, A. Suslu, Y. Chen, C. Ko, J. Park, K. Liu, J. Li, K. Kippalgaonkar, J. J. Urban, S. Tongay, J. Wu, *Nat. Commun.* **2015**, *6*, 8573.
- [86] S. G. Jeon, H. Shin, Y. H. Jaung, J. Ahn, J. Y. Song, Nanoscale 2018, 10, 5985.
- [87] H. Jang, J. D. Wood, C. R. Ryder, M. C. Hersam, D. G. Cahill, Adv. Mater. 2015, 27, 8017.
- [88] B. Sun, X. Gu, Q. Zeng, X. Huang, Y. Yan, Z. Liu, R. Yang, Y. K. Koh, Adv. Mater. 2017, 29, 1603297.
- [89] Z. Luo, J. Maassen, Y. Deng, Y. Du, R. P. Garrelts, M. S. Lundstrom, D. Y. Peide, X. Xu, Nat. Commun. 2015, 6, 8572.
- [90] J. Zhu, H. Park, J. Y. Chen, X. Gu, H. Zhang, S. Karthikeyan, N. Wendel, S. A. Campbell, M. Dawber, X. Du, M. Li, J.-P. Wang, R. Yang, X. Wang, Adv. Electron. Mater. 2016, 2, 1600040.
- [91] Y. Zhao, G. Zhang, M. H. Nai, G. Ding, D. Li, Y. Liu, K. Hippalgaonkar, C. T. Lim, D. Chi, B. Li, J. Wu, J. T. L. Thong, *Adv. Mater.* **2018**, *30*, 1804928.
- [92] W. Xu, G. Zhang, J. Phys.: Condens. Matter 2016, 28, 175401.
- [93] Y. Chen, C. Chen, R. Kealhofer, H. Liu, Z. Yuan, L. Jiang, J. Suh, J. Park, C. Ko, H. S. Choe, J. Avila, M. Zhong, Z. Wei, J. Li, S. Li, H. Gao, Y. Liu, J. Analytis, Q. Xia, M. C. Asensio, J. Wu, *Adv. Mater.* **2018**, *30*, 1800754.
- [94] M. Zhong, Q. Xia, L. Pan, Y. Liu, Y. Chen, H. X. Deng, J. Li, Z. Wei, Adv. Funct. Mater. 2018, 28, 1802581.
- [95] G. Qin, X. Zhang, S. Yue, Z. Qin, H. Wang, Y. Han, M. Hu, Phys. Rev. B 2016, 94, 165445.
- [96] Y. Hong, J. Zhang, X. Huang, X. C. Zeng, Nanoscale 2015, 7, 18716.
- [97] B. Smith, B. Vermeersch, J. Carrete, E. Ou, J. Kim, N. Mingo, D. Akinwande, L. Shi, Adv. Mater. 2017, 29, 1603756.
- [98] S. R. Tamalampudi, Y.-Y. Lu, R. Kumar U, R. Sankar, C.-D. Liao, K. Moorthy B, C.-H. Cheng, F. C. Chou, Y.-T. Chen, *Nano Lett.* 2014, 14, 2800.



ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [99] W. Feng, W. Zheng, W. Cao, P. Hu, Adv. Mater. 2014, 26, 6587.
- [100] Y. T. Huang, C. W. Huang, J. Y. Chen, Y. H. Ting, K. C. Lu, Y. L. Chueh, W. W. Wu, ACS Nano 2014, 8, 9457.
- [101] H. Zhou, Y. Cai, G. Zhang, Y.-W. Zhang, Nanoscale 2018, 10, 480.
- [102] M. T. Pettes, J. Maassen, I. Jo, M. S. Lundstrom, L. Shi, Nano Lett. 2013, 13, 5316.
- [103] B. Qiu, X. Ruan, Appl. Phys. Lett. 2010, 97, 183107.
- [104] X. Tao, Y. Gu, Nano Lett. 2013, 13, 3501.
- [105] S. Zhou, X. Tao, Y. Gu, J. Phys. Chem. C 2016, 120, 4753.
- [106] J. Chen, G. Zhang, B. Li, Nanoscale 2013, 5, 532.
- [107] T. Zhao, Y. Sun, Z. Shuai, D. Wang, Chem. Mater. 2017, 29, 6261.
- [108] F. Q. Wang, S. Zhang, J. Yu, Q. Wang, Nanoscale 2015, 7, 15962.
- [109] L. D. Zhao, S. H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* **2014**, *508*, 373.
- [110] L. D. Zhao, C. Chang, G. Tan, M. G. Kanatzidis, *Energy Environ. Sci.* 2016, 9, 3044.
- [111] L.-C. Zhang, G. Qin, W.-Z. Fang, H.-J. Cui, Q.-R. Zheng, Q.-B. Yan, G. Su, Sci. Rep. 2016, 6, 19830.
- [112] C. Zhang, H. Yin, M. Han, Z. Dai, H. Pang, Y. Zheng, Y. Q. Lan, J. Bao, J. Zhu, ACS Nano 2014, 8, 3761.
- [113] L. Li, Z. Chen, Y. Hu, X. Wang, T. Zhang, W. Chen, Q. Wang, J. Am. Chem. Soc. 2013, 135, 1213.
- [114] G. Qin, Z. Qin, W.-Z. Fang, L.-C. Zhang, S.-Y. Yue, Q.-B. Yan, M. Hu, G. Su, *Nanoscale* **2016**, *8*, 11306.
- [115] E. J. Skoug, D. T. Morelli, Phys. Rev. Lett. 2011, 107, 235901.
- [116] G. Qin, Z. Qin, H. Wang, M. Hu, Nano Energy 2018, 50, 425.
- [117] S. Lee, K. Esfarjani, T. Luo, J. Zhou, Z. Tian, G. Chen, Nat. Commun. 2014, 5, 3525.
- [118] C. W. Li, J. Hong, A. F. May, D. Bansal, S. Chi, T. Hong, G. Ehlers, O. Delaire, *Nat. Phys.* **2015**, *11*, 1063.
- [119] T. Pandey, D. S. Parker, L. Lindsay, Nanotechnology 2017, 28, 455706.
- [120] A. S. Nissimagoudar, J. Ma, Y. Chen, W. Li, J. Phys.: Condens. Matter 2017, 29, 335702.
- [121] H. Wang, G. Qin, J. Yang, Z. Qin, Y. Yao, Q. Wang, M. Hu, J. Appl. Phys. 2019, 125, 245104.
- [122] E. T. Swartz, R. O. Pohl, Rev. Mod. Phys. 1989, 61, 605.
- [123] A. Rajabpour, S. Vaez Allaei, F. Kowsary, Appl. Phys. Lett. 2011, 99, 051917.
- [124] X. Liu, G. Zhang, Y.-W. Zhang, Nano Res. 2016, 9, 2372.
- [125] P. E. Hopkins, ISRN Mech. Eng. 2013, 2013, 1.
- [126] P. Zhang, P. Yuan, X. Jiang, S. Zhai, J. Zeng, Y. Xian, H. Qin, D. Yang, Small 2018, 14, 1702769.
- [127] H. Zhou, G. Zhang, Chin. Phys. B 2018, 27, 034401.
- [128] S. Ghatak, A. N. Pal, A. Ghosh, ACS Nano 2011, 5, 7707.
- [129] M. Mahjouri-Samani, M.-W. Lin, K. Wang, A. R. Lupini, J. Lee, L. Basile, A. Boulesbaa, C. M. Rouleau, A. A. Puretzky, I. N. Ivanov, K. Xiao, M. Yoon, D. B. Geohegan, *Nat. Commun.* **2015**, *6*, 7749.
- [130] Z. Wang, Y. Xie, H. Wang, R. Wu, T. Nan, Y. Zhan, J. Sun, T. Jiang, Y. Zhao, Y. Lei, M. Yang, W. Wang, Q. Zhu, X. Ma, Y. Hao, *Nanotechnology* **2017**, *28*, 325602.
- [131] Y. K. Koh, S. L. Singer, W. Kim, J. M. Zide, H. Lu, D. G. Cahill, A. Majumdar, A. C. Gossard, J. Appl. Phys. 2009, 105, 054303.
- [132] H.-C. Chien, D.-J. Yao, M.-J. Huang, T.-Y. Chang, *Rev. Sci. Instrum.* 2008, 79, 054902.
- [133] C.-C. Chen, Z. Li, L. Shi, S. B. Cronin, Appl. Phys. Lett. 2014, 104, 081908.
- [134] W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, R. S. Ruoff, Nano Lett. 2010, 10, 1645.
- [135] J. Judek, A. P. Gertych, M. Świniarski, A. Łapińska, A. Dużyńska, M. Zdrojek, *Sci. Rep.* **2015**, *5*, 12422.
- [136] E. Yalon, O. z. r. B. Aslan, K. K. Smithe, C. J. McClellan, S. V. Suryavanshi, F. Xiong, A. Sood, C. M. Neumann, X. Xu, K. E. Goodson, ACS Appl. Mater. Interfaces 2017, 9, 43013.

- [137] Y. Liu, Z.-Y. Ong, J. Wu, Y. Zhao, K. Watanabe, T. Taniguchi, D. Chi, G. Zhang, J. T. Thong, C.-W. Qiu, K. Hippalgaonkar, *Sci. Rep.* **2017**, 7, 43886.
- [138] P. Yuan, C. Li, S. Xu, J. Liu, X. Wang, Acta Mater. 2017, 122, 152.
- P. Yasaei, C. J. Foss, K. Karis, A. Behranginia, A. I. El-Ghandour,
 A. Fathizadeh, J. Olivares, A. K. Majee, C. D. Foster,
 F. Khalili-Araghi, Z. Aksamija, A. Salehi-Khojin, *Adv. Mater. Interfaces* 2017, 4, 1700334.
- [140] X. Liu, J. Gao, G. Zhang, Y.-W. Zhang, Nano Res. 2017, 10, 2944.
- [141] A. Behranginia, Z. Hemmat, A. K. Majee, C. J. Foss, P. Yasaei, Z. Aksamija, A. Salehi-Khojin, ACS Appl. Mater. Interfaces 2018, 10, 24892.
- [142] A. Allain, J. Kang, K. Banerjee, A. Kis, Nat. Mater. 2015, 14, 1195.
- [143] R. Mao, B. D. Kong, K. W. Kim, J. Appl. Phys. 2014, 116, 034302.
- [144] L. Wang, I. Meric, P. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. Campos, D. Muller, J. Guo, P. Kim, J. Hone, K. L. Shepard, C. R. Dean, *Science* **2013**, *342*, 614.
- [145] W. Liu, J. Kang, W. Cao, D. Sarkar, Y. Khatami, D. Jena, K. Banerjee, in *IEEE Int. Electron Dev. Meet.*, IEEE, Washington, DC 2013, pp. 19.4.1–19.4.4.
- [146] E. Landry, A. McGaughey, Phys. Rev. B 2009, 80, 165304.
- [147] C. A. da Cruz, P. Chantrenne, X. Kleber, J. Heat Transfer 2012, 134, 062402.
- [148] N. Yang, T. Luo, K. Esfarjani, A. Henry, Z. Tian, J. Shiomi, Y. Chalopin, B. Li, G. Chen, J. Comput. Theor. Nanosci. 2015, 12, 168.
- [149] Y. Wang, X. Ruan, A. K. Roy, Phys. Rev. B 2012, 85, 205311.
- [150] R. Mao, B. Kong, C. Gong, S. Xu, T. Jayasekera, K. Cho, K. Kim, *Phys. Rev. B* 2013, *87*, 165410.
- [151] P. Pichanusakorn, P. Bandaru, Mater. Sci. Eng., R 2010, 67, 19.
- [152] G. Ding, J. He, Z. Cheng, X. Wang, S. Li, J. Mater. Chem. C 2018, 6, 13269.
- [153] J. He, T. M. Tritt, Science 2017, 357, eaak9997.
- [154] H. S. Kim, W. S. Liu, G. Chen, C. W. Chu, Z. F. Ren, Proc. Natl. Acad. Sci. USA 2015, 112, 8205.
- [155] G. J. Snyder, M. Christensen, E. Nishibori, T. Caillat, B. B. Iversen, *Nat. Mater.* 2004, *3*, 458.
- [156] J. Crossno, J. K. Shi, K. Wang, X. Liu, A. Harzheim, A. Lucas, S. Sachdev, P. Kim, T. Taniguchi, K. Watanabe, T. A. Ohki, K. C. Fong, *Science* **2016**, *351*, 1058.
- [157] N. Wakeham, A. F. Bangura, X. Xu, J.-F. Mercure, M. Greenblatt, N. E. Hussey, *Nat. Commun.* **2011**, *2*, 396.
- [158] L. Hicks, M. S. Dresselhaus, Phys. Rev. B 1993, 47, 12727.
- [159] J. Pu, K. Kanahashi, N. T. Cuong, C.-H. Chen, L.-J. Li, S. Okada, H. Ohta, T. Takenobu, *Phys. Rev. B* **2016**, *94*, 014312.
- [160] H. Babaei, J. Khodadadi, S. Sinha, Appl. Phys. Lett. 2014, 105, 193901.
- [161] D. Fan, H. Liu, L. Cheng, P. Jiang, J. Shi, X. Tang, Appl. Phys. Lett. 2014, 105, 133113.
- [162] G. Ding, M. Wei, G. Surucu, Z. Liang, X. Wang, Appl. Surf. Sci. 2019, 491, 750.
- [163] M. Buscema, M. Barkelid, V. Zwiller, H. S. van der Zant, G. A. Steele, A. Castellanos-Gomez, *Nano Lett.* 2013, 13, 358.
- [164] J. Wu, H. Schmidt, K. K. Amara, X. Xu, G. Eda, B. Özyilmaz, Nano Lett. 2014, 14, 2730.
- [165] M. Kayyalha, J. Maassen, M. Lundstrom, L. Shi, Y. P. Chen, J. Appl. Phys. 2016, 120, 134305.
- [166] K. Hippalgaonkar, Y. Wang, Y. Ye, D. Y. Qiu, H. Zhu, Y. Wang, J. Moore, S. G. Louie, X. Zhang, *Phys. Rev. B* 2017, *95*, 115407.
- [167] J. Wu, Y. Liu, Y. Liu, Y. Cai, Y. Zhao, H. K. Ng, K. Watanabe, T. Taniguchi, G. Zhang, C. Qiu, D. Chi, A. H. Castro Neto, J. T. L. Thong, K. P. Loh, K. Hippalgaonkar, Kondo Impurities in Two Dimensional MoS2 for Achieving Ultrahigh Thermoelectric Powerfactor, **2019**, arXiv:1901, 04661.



www.afm-journal.de

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [168] M. Yoshida, T. Iizuka, Y. Saito, M. Onga, R. Suzuki, Y. Zhang, Y. Iwasa, S. Shimizu, *Nano Lett.* **2016**, *16*, 2061.
- [169] R. Fei, A. Faghaninia, R. Soklaski, J.-A. Yan, C. Lo, L. Yang, Nano Lett. 2014, 14, 6393.
- [170] S. J. Choi, B.-K. Kim, T.-H. Lee, Y. H. Kim, Z. Li, E. Pop, J.-J. Kim, J. H. Song, M.-H. Bae, *Nano Lett.* **2016**, *16*, 3969.
- [171] H. Liu, H. S. Choe, Y. Chen, J. Suh, C. Ko, S. Tongay, J. Wu, Appl. Phys. Lett. 2017, 111, 102101.
- [172] C. Wan, X. Gu, F. Dang, T. Itoh, Y. Wang, H. Sasaki, M. Kondo, K. Koga, K. Yabuki, G. J. Snyder, R. Yang, K. Koumoto, *Nat. Mater.* 2015, *14*, 622.
- [173] N. T. Hung, A. R. Nugraha, R. Saito, Appl. Phys. Lett. 2017, 111, 092107.
- [174] T. Harman, D. Spears, M. Manfra, J. Electron. Mater. 1996, 25, 1121.
- [175] T. Harman, P. Taylor, M. Walsh, B. LaForge, Science 2002, 297, 2229.
- [176] J. Zeng, X. He, S.-J. Liang, E. Liu, Y. Sun, C. Pan, Y. Wang, T. Cao, X. Liu, C. Wang, L. Zhang, S. Yan, G. Xu, Z. Wang, K. Watanabe, T. Taniguchi, D. J. Singh, L. Zhang, F. Miao, *Nano Lett.* **2018**, *18*, 7538.
- [177] N. T. Hung, E. H. Hasdeo, A. R. Nugraha, M. S. Dresselhaus, R. Saito, Phys. Rev. Lett. 2016, 117, 036602.
- [178] J.-S. Rhyee, K. H. Lee, S. M. Lee, E. Cho, S. I. Kim, E. Lee, Y. S. Kwon, J. H. Shim, G. Kotliar, *Nature* **2009**, *459*, 965.
- [179] Y. Cai, G. Zhang, Y.-W. Zhang, J. Am. Chem. Soc. 2014, 136, 6269.
- [180] D. Kozawa, R. Kumar, A. Carvalho, K. K. Amara, W. Zhao, S. Wang, M. Toh, R. M. Ribeiro, A. C. Neto, K. Matsuda, G. Eda, *Nat. Commun.* 2014, 5, 4543.
- [181] N. Kumar, J. He, D. He, Y. Wang, H. Zhao, J. Appl. Phys. 2013, 113, 133702.
- [182] H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, L. Huang, ACS Nano 2013, 7, 1072.
- [183] L. Wang, C. Xu, M.-Y. Li, L.-J. Li, Z.-H. Loh, Nano Lett. 2018, 18, 5172.
- [184] Z. Chi, H. Chen, Z. Chen, Q. Zhao, H. Chen, Y.-X. Weng, ACS Nano 2018, 12, 8961.
- [185] Z. Nie, R. Long, L. Sun, C.-C. Huang, J. Zhang, Q. Xiong, D. W. Hewak, Z. Shen, O. V. Prezhdo, Z.-H. Loh, ACS Nano 2014, 8, 10931.

- [186] M. Selig, G. Berghäuser, A. Raja, P. Nagler, C. Schüller, T. F. Heinz, T. Korn, A. Chernikov, E. Malic, A. Knorr, *Nat. Commun.* 2016, 7, 13279.
- [187] S. Mouri, Y. Miyauchi, K. Matsuda, Nano Lett. 2013, 13, 5944.
- [188] A. M. Jones, H. Yu, N. J. Ghimire, S. Wu, G. Aivazian, J. S. Ross, B. Zhao, J. Yan, D. G. Mandrus, D. Xiao, *Nat. Nanotechnol.* **2013**, *8*, 634.
- [189] A. Thilagam, J. Appl. Phys. 2016, 120, 124306.
- [190] A. Thilagam, J. Appl. Phys. 2016, 119, 164306.
- [191] T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler, C. Schüller, Appl. Phys. Lett. 2011, 99, 102109.
- [192] W. Xu, G. Zhang, B. Li, J. Appl. Phys. 2014, 116, 134303.
- [193] G. Zhang, Y.-W. Zhang, Mech. Mater. 2015, 91, 382.
- [194] D. Li, J. He, G. Ding, Q. Tang, Y. Ying, J. He, C. Zhong, Y. Liu, C. Feng, Q. Sun, H. Zhou, P. Zhou, G. Zhang, *Adv. Funct. Mater.* 2018, 28, 1801685.
- [195] H. Xie, T. Ouyang, É. Germaneau, G. Qin, M. Hu, H. Bao, Phys. Rev. B 2016, 93, 075404.
- [196] B. Liao, J. Zhou, B. Qiu, M. S. Dresselhaus, G. Chen, Phys. Rev. B 2015, 91, 235419.
- [197] B. Liao, B. Qiu, J. Zhou, S. Huberman, K. Esfarjani, G. Chen, Phys. Rev. Lett. 2015, 114, 115901.
- [198] M. Terraneo, M. Peyrard, G. Casati, Phys. Rev. Lett. 2002, 88, 094302.
- [199] B. Li, L. Wang, G. Casati, Phys. Rev. Lett. 2004, 93, 184301.
- [200] N. Yang, G. Zhang, B. Li, Appl. Phys. Lett. 2009, 95, 033107.
- [201] J. Hu, X. Ruan, Y. P. Chen, Nano Lett. 2009, 9, 2730.
- [202] H. Tian, D. Xie, Y. Yang, T.-L. Ren, G. Zhang, Y.-F. Wang, C.-J. Zhou, P.-G. Peng, L.-G. Wang, L.-T. Liu, *Sci. Rep.* **2012**, *2*, 523.
- [203] G. Zhang, H. Zhang, Nanoscale 2011, 3, 4604.
- [204] H. Wang, S. Hu, K. Takahashi, X. Zhang, H. Takamatsu, J. Chen, *Nat. Commun.* 2017, 8, 15843.
- [205] X. Liu, G. Zhang, Y.-W. Zhang, Nano Res. 2015, 8, 2755.
- [206] A. Sood, F. Xiong, S. Chen, H. Wang, D. Selli, J. Zhang, C. J. McClellan, J. Sun, D. Donadio, Y. Cui, *Nat. Commun.* **2018**, *9*, 4510.
- [207] S. Hu, Z. Zhang, Z. Wang, K. Zeng, Y. Cheng, J. Chen, G. Zhang, Energy Environ. Mater. 2018, 7, 12.

