Effect of dimensionality on thermoelectric powerfactor of molybdenum disulfide

H. K. Ng, D. Chi, and K. Hippalgaonkar

Citation: Journal of Applied Physics 121, 204303 (2017); doi: 10.1063/1.4984138
View online: http://dx.doi.org/10.1063/1.4984138
View Table of Contents: http://aip.scitation.org/toc/jap/121/20
Published by the American Institute of Physics

Articles you may be interested in

Photoinduced quantum spin/valley Hall effect and its electrical manipulation in silicene
Journal of Applied Physics 121, 205106 (2017); 10.1063/1.4983819

Effects of torsion on the thermal conductivity of multi-layer graphene
Journal of Applied Physics 121, 205102 (2017); 10.1063/1.4983812

A balance equations approach for the study of the dynamic response and electronic noise in graphene
Journal of Applied Physics 121, 185705 (2017); 10.1063/1.4983190

Hybrid mode cesium diode thermionic converter
Journal of Applied Physics 121, 203304 (2017); 10.1063/1.4983816

High-temperature thermal conductivity of thermoelectric clathrates
Journal of Applied Physics 121, 205105 (2017); 10.1063/1.4983817

Thermoelectric properties of Si/CoSi2 sub-micrometer composites prepared by melt-spinning technique
Journal of Applied Physics 121, 205107 (2017); 10.1063/1.4983776
Effect of dimensionality on thermoelectric powerfactor of molybdenum disulfide

H. K. Ng, D. Chi, and K. Hippalgaonkar

Institute of Materials Research and Engineering, #08-03, 2 Fusionopolis Way, Agency for Science, Technology and Research, Singapore 138634

(Received 2 February 2017; accepted 13 May 2017; published online 31 May 2017)

We present that two-dimensional (2D) bilayer molybdenum disulfide (MoS2) exhibits an enhanced Seebeck coefficient over its three-dimensional (3D) counterpart arising from dimensionality confinement. It has been predicted that quantum confinement enhances thermoelectric performance but no studies have focused on a single material to present a theoretical and experimental comparison, which would illustrate the enhancement of thermoelectric performance. Layered MoS2 provides an opportunity to verify this hypothesis and in this work, we extensively study the Seebeck coefficient, \( S \), the electrical conductivity, \( \sigma \), and the thermoelectric powerfactor, \( S^2\sigma \) of 2D monolayer and bilayer MoS2 using theoretical Boltzmann Transport Equation calculations and compare the results to well-characterized experimental data. We conclude that dimensional confinement indeed enhances the Seebeck coefficient by up to \( \sim 50\% \) in 2D bilayer MoS2 over 3D MoS2 under similar doping concentrations because of the discretization of density of states. We also consider electrical conductivity with various energy-dependent scattering rates considering charged-impurities and acoustic phonon mediated scattering, and comment on a theoretical comparison of the powerfactor to the best-case scenario for 3D MoS2.

Published by AIP Publishing.

[http://dx.doi.org/10.1063/1.4984138]

I. INTRODUCTION

Research on thermoelectric materials centers around improving the thermoelectric efficiency in order to achieve wide practical applications. The efficiency of a thermoelectric material is governed by the thermoelectric figure of merit, \( ZT = S^2\sigma T / (\kappa_e + \kappa_L) \) where the thermoelectric properties \( S, \sigma, T, \kappa_e, \) and \( \kappa_L \) represent the Seebeck coefficient, electrical conductivity, thermodynamic temperature, and electronic and lattice thermal conductivity, respectively. Thus far, a large spectrum of methods have been investigated and demonstrated to improve thermoelectric performance such as the optimization of carrier concentration,\(^1\) alloying,\(^2,3\) and quantum confinement through nanostructuring.\(^4,5\) Previously, quantum confinement achieved using quantum-well structures was shown to be capable of improving the thermoelectric performance of bulk Bi2Te3,\(^4\) and experimentally demonstrated in superlattice p-type Bi2Te3/Sb2Te3 samples,\(^9\) although this has not been repeated since. Theoretical models have also shown that lowering the dimensionality of a material could improve thermoelectric performance,\(^10\) and that there exists an optimal Seebeck coefficient corresponding to the maximized thermoelectric powerfactor of a material at any given temperature.\(^11\) Two theoretical models, namely the Boltzmann Transport Equation (BTE) and Landauer Formalism, have been commonly used to study the optimization of thermoelectric properties. With the discovery of van der Waals 2-dimensional (2D) materials where carriers (electrons or holes) are naturally restricted to two dimensions, there is great potential in optimizing thermoelectric performance through quantum (dimensionality) confinement with small variation in the quantum well thickness.\(^12\) However, studies on thermoelectric optimization thus far have mainly been comparisons between calculations of 3-, 2-, and/or 1-dimensional (3D, 2D, and 1D) materials using either the BTE\(^4,11,13,14\) or Landauer\(^10,15,16\) models without accounting for energy dependence of scattering and experimental reports on 2D thermoelectric materials.\(^17,18\) In this paper, we focus on molybdenum disulfide (MoS2), a prototypical 2D transition metal dichalcogenide (TMD) semiconductor, which has been demonstrated to exhibit large Seebeck coefficients and power factor\(^17-19\) due to large effective mass, valley degeneracy, and carrier confinement.\(^20-22\) We perform BTE calculations and compare with well-characterized monolayer and bilayer MoS2 experimental data and we conclude that bilayer MoS2 exhibits a higher thermoelectric powerfactor \( (S^2\sigma) \) over monolayer and 3D MoS2 and also consider the effect of energy dependence of scattering for both two and three dimensions. Our detailed BTE calculations assume (a) single-band material and (b) parabolic band structure with a well-defined effective mass. Due to the lack of experimental data on 3D MoS2 at similar doping levels, we assume a best-case scenario where the equivalent carrier concentration is the same for 3D as it is for experimentally measured bilayer MoS2, and compare to previously measured mobility at this carrier concentration. One would expect that similar levels of doping in 3D MoS2 will most likely result in shorter scattering times due to charged impurity (CI) scattering,\(^23,24\) which we show is not present in 2D MoS2 backgated devices therefore delineating the advantage of such 2D-based systems.

\(^a\)Author to whom correspondence should be addressed: kedarh@imre.a-star.edu.sg
II. APPROACH

For a comprehensive comparison with our theoretical BTE calculations, we used monolayer and bilayer molybdenum disulfide (MoS\(_2\)) thermoelectric experimental data measured under vacuum at room temperature (300 K) using the field-effect doping technique. Details and results of the experiment can be found in Ref. 17. The Seebeck coefficient and electrical conductivity of 2D MoS\(_2\) are measured as a function of carrier concentration tuned via a backgate as shown in Fig. 1. The carrier concentration is given as

\[ n = C_{\text{ox}}(V_g - V_i), \]

where \( C_{\text{ox}} \) is the capacitance between the channel and the back gate \((1.26 \times 10^{-4} \text{F/m}^2)\), \( e \) is the electron charge \((1.6 \times 10^{-19} \text{C})\), and \( V_g \) and \( V_i \) are the gate and threshold voltage, respectively.\(^{17}\)

Theoretically, the steady-state solution to the linearized BTE determines the thermoelectric transport coefficients and is given as

\[ S = \frac{k_B}{e} \left[ \eta - \left( \frac{r + D}{2} + 1 \right) F_{r+(D/2)}(\eta) \right], \]

\[ n = \frac{N_e}{g_D a^3 d^2} \left( \frac{2k_BT}{h^2} \right)^{D/2} F_{(D/2)-1}(\eta), \]

where \( g_D = \left\{ \begin{array}{ll} 2\pi^2 & (\text{for } D = 3) \\ 2\pi & (\text{for } D = 2) \end{array} \right. \)

where \( S \) and \( n \) are the Seebeck coefficient and carrier concentration, respectively. The electrical conductivity (\( \sigma \)) is given as

\[ \sigma = \frac{N_e e^2 \epsilon_0}{g_D a^3 d^2 m^* (2m^* e)^{D/2}} \left( \frac{2\pi}{h^2} \right)^{D/2} F_{r+(D/2)} \left( \frac{2\pi}{D} + 1 \right) F_{r+(D/2)-1}(\eta). \]

Here, \( F_i(\eta) = \int_{\eta}^{\infty} [\sqrt{\pi} \exp(x - \eta) + 1] \text{d}x \) is the \( i \)-th order Fermi integral and is evaluated through numerical integration.\(^{26}\) and \( \eta = (E_F - E_C)/k_B T \) is the reduced Fermi potential, where \( E_F \) is the Fermi energy and \( E_C \) is the conduction band minimum (CBM). Since transport through 2D MoS\(_2\) is n-type,\(^{27,28}\) we only consider n-type transport through the conduction band. The optical bandgap for monolayer MoS\(_2\) is \( \sim 1.8 \text{ eV} \) (Refs. 20 and 28) and for bilayer/3D MoS\(_2\) is \( \sim 1.2 \text{ eV} \) (Refs. 21 and 29), where the quasiparticle (QP) bandgap for monolayer and bilayer MoS\(_2\) is \( \sim 2.7 \text{ eV} \) and \( \sim 2 \text{ eV} \) according to calculated QP band structures, respectively.\(^{17,30}\) Hence, the bandgap is large enough at 300 K that transport is purely due to electrons. \( N_e, m^*, D, r, \tau_0, \) and \( a \) represent the number of conduction valleys \((N_e = 6, 6, 2 \text{ for 3D, bilayer, and monolayer MoS}_2, \text{respectively})\), band effective mass, dimensionality factor \((D = 3, 2 \text{ for 3D material, 2D samples})\), scattering parameter, scattering time constant, and relevant length scale (e.g., quantum well or layer thickness) of the device under consideration, respectively. \( k_B \) and \( h \) are the Boltzmann and reduced Planck constants.

In order to determine the Seebeck coefficient for the monolayer and bilayer MoS\(_2\) samples, the position of the Fermi level, \( E_F \) with respect to the conduction band minimum (CBM), \( E_C \) must be calculated. This is also known as the Fermi potential given as \( E_F - E_C \). The field-effect doping technique can push the doping into the degenerate limit \(|E_F - E_C| \leq 2k_BT\)\(^{31}\) where transport occurs through the band density of states (DOS) and Fermi-Dirac statistics need to be used. Therefore, in the degenerate limit, the carrier concentration is given as

\[ n = \int_{E_C}^{\infty} D_{2D}(E)f_{FD}(E)\text{d}E, \]

where \( D_{2D}(E) = g_\text{e}g_\text{m}m^*/2\pi h^2 \) are the 2D density of states (DOS) and is energy-independent, and \( f_{FD} \) is the Fermi-Dirac distribution function. Here, \( g_\text{e} \) and \( g_\text{m} \) are the valley and spin degeneracies, respectively. The effective masses for monolayer and bilayer MoS\(_2\) are 0.52 \( m_0 \) and 0.68 \( m_0 \), where \( m_0 \) is the free electron mass \((9.109 \times 10^{-31} \text{ kg})\) and their respective \( D_{2D} \) are \( 4.33 \times 10^{13} \text{ cm}^{-2}\text{eV}^{-1} \) and \( 17.0 \times 10^{13} \text{ cm}^{-2}\text{eV}^{-1} \).\(^{17}\) Due to the larger effective mass and higher valley degeneracy, bilayer MoS\(_2\) has a larger \( D_{2D} \) compared to monolayer MoS\(_2\).

The Fermi-Dirac distribution is given as

\[ f_{FD}(E) = \frac{1}{\exp((E-E_F)/k_BT) + 1}. \]

Letting \( \epsilon = (E - E_F)/k_BT \) and \( \eta = (E_F - E_C)/k_BT \), we can rewrite Eq. (5) as

\[ n_{2D} = N_{2D} \int_{0}^{\infty} f_{FD}(\epsilon)\text{d}\epsilon, \]
where $N_{C,2D} = D_{2D} \times k_B T$ is the 2D effective density of states. In this case, \( \int_0^\infty f_{FD}(\varepsilon) \, d\varepsilon = F_0(\eta_F) \) is the 0th-order Fermi integral and can be evaluated analytically as \( F_0(\eta_F) = \ln(1 + \exp^{\eta_F}) \). Combining \( F_0(\eta_F) \) into Eq. (7), we obtain

\[
E_F - E_C = k_B T \times \ln\left(\exp^{n_{2D}/N_{C,2D}} - 1\right),
\]

where \( n_{2D} \) can be a theoretical value or experimentally determined. The carrier concentration of 3D MoS\(_2\) is given by

\[
n_{3D} = \frac{2}{e^2} \int_0^\infty N_{C,3D} \sqrt{\varepsilon} f_{FD}(\varepsilon) \, d\varepsilon,
\]

where \( N_{C,3D} = 12(2\pi m^* k_B T/k)^{3/2} \) is the 3D effective density of states, and the 3D effective mass is 0.53 \( m_0 \). Here, \( \int_0^\infty f_{FD}(\varepsilon) \, d\varepsilon \) reduces to a half-order Fermi integral, \( F_{1/2}(\eta_F) \) and can only be evaluated numerically. For ease of comparison between \( n_{2D} \) and \( n_{3D} \), we multiply \( n_{3D} \) by the thickness of a bilayer MoS\(_2\) \((2 \times t_{MoS2} = 1.3 \text{ nm})\) to obtain its equivalent carrier concentration in 2D. The respective \( E_F - E_C \) for monolayer and bilayer MoS\(_2\) are plotted against their carrier concentration \( n \) in Fig. 2(a), and doping is seen to be more effective in 3D MoS\(_2\) as compared to 2D MoS\(_2\). The shaded regions in Fig. 2(a) represent the widths of the window function, given by \( F_{wa}(E,T) = (E - E_F) \times [-dF(E,T)/dE] \) in the degenerate limit, where the respective 2D or 3D DOS are accessible for the Seebeck coefficient. The lighter-shaded gray region has a width of \(~2 \text{ kg} T \) \((~52 \text{ meV})\) and the darker-shaded gray region has a width of \(~2.8 \text{ kg} T \) \((~74 \text{ meV})\) from \( E - E_F = 0 \), corresponding to the peak of the local maxima and its full-width-half-maximum (FWHM), respectively.

### III. RESULTS

In this section, we determine the dominating scattering mechanism present in the MoS\(_2\) samples at room temperature, and compare their electrical conductivity, Seebeck coefficient, and thermoelectric power factor. Different scattering mechanisms affecting carrier transport in 3D and 2D MoS\(_2\) samples are shown in Table I.17,25,31,34

Since the electrical conductivity in the degenerate limit is given by \( \sigma = n e \mu = n e^2 \tau / m^* \), the scattering time constant \( \tau \) can be computed over all doping concentrations, \( n \) from the 2D MoS\(_2\) experimental data in the ON state at \(~1.4 \times 10^{13} \text{ cm}^{-2} \) and \(~5.2 \times 10^{13} \text{ cm}^{-2} \) for the monolayer and bilayer MoS\(_2\), respectively. The scattering time constant for both 2D MoS\(_2\) \((\tau_{0,ML} \text{ and } \tau_{0,BL})\), assuming constant relaxation time approximation, can then be determined by taking average of the calculated scattering time constants from the calculated electrical conductivity for the BTE model in Eq. (4). The scattering time constant for monolayer and bilayer MoS\(_2\) is \( \tau_{0,ML} = 6.77 \times 10^{-15} \text{ s} \) and \( \tau_{0,BL} = 2.71 \times 10^{-14} \text{ s} \), comparable to literature values for n-type MoS\(_2\) calculated from first-principles.27,35 Figure 2(b) shows that our experimental electrical conductivity indeed fits the BTE model very well at \( r = 0 \), revealing that acoustic phonon (AP) scattering and/or intervalley scattering are the dominant scattering mechanisms affecting electron transport in these MoS\(_2\) samples at room temperature and, as is seen later, is well corroborated by the fit to the Seebeck coefficient. Note that intervalley scattering is phonon-mediated as well and hence energy-independent \((r = 0)\), which can reduce carrier transport at high temperatures and especially for heavy effective mass electrons due to the thermal broadening of the Fermi distribution \((\sim2k_B T)\). As expected, the electrical conductivity \( (\sigma_{ML} \text{ and } \sigma_{BL}) \) of MoS\(_2\) samples increases via back-gate biasing (field-effect doping) since it increases the carrier concentration, \( n \). Although in the monolayer MoS\(_2\), electrons are also confined to two dimensions, it has a lower density of states and a lower valley degeneracy \((\gamma_\text{L})\) of 2 as compared to 6 in the bilayer, resulting in an electrical conductivity \( \sigma_{BL} \) about 50% lower than \( \sigma_{ML} \). A calculation using Eq. (9) for the electrical conductivity in 3D MoS\(_2\) \((\sigma_{3D})\) under pure acoustic phonon scattering, assuming that the scattering

![Image](image60x176to288x432)

**FIG. 2.** (a) The tuning of carrier concentration against the Fermi potential, \( E_F - E_C \), for all MoS\(_2\) samples. The window function is outlined by the shaded regions, where the Seebeck coefficient will be maximized. The lighter-shaded region represents the range from the local maxima and local minima, while the darker-shaded region stretches the full-width-half-maximum (FWHM) of the window function: \( F_{wa}(E,T) \). (b) Experimental electrical conductivity data of monolayer and bilayer MoS\(_2\) samples are plotted with our BTE calculations. The experimental data fit our calculations very well for a scattering parameter, \( r = 0 \), where the energy-dependent scattering time is given by \( \tau = \tau_0 \times E^r \), revealing that acoustic phonon scattering is likely dominant in 2D MoS\(_2\) samples for both the monolayer and bilayer. The electrical conductivity for 3D MoS\(_2\) is calculated using the upper limit of mobility, \( \mu_{ub} = 170 \text{ cm}^2/\text{Vs} \).
times are the same in bilayer and 3D, revealed a $\sigma_{3D}$ that is one order of magnitude higher than $\sigma_{BL}$, which is highly impossible in similar highly doped 3D semiconductors.\textsuperscript{23,38} Hence, in order to obtain the realistic estimates of $\sigma_{3D}$ for 3D MoS$_2$, its value of mobility ($\mu_{3D}$) under similar carrier concentrations ($\sim 10^{20}$ cm$^{-3}$) at room temperature is required. Previously, the mobility of undoped 3D MoS$_2$ was calculated to be $\sim 100$ cm$^2$/Vs at a much lower carrier concentration of about $1.25 \times 10^{16}$ cm$^{-3}$ by Fivaz and Mooser.\textsuperscript{39}

So far, only an indirect estimation of $\mu_{3D}$ using transient absorption microscopy has been performed by Kumar et al. where intervalley scattering is dominant ($r = 0$).\textsuperscript{40} They obtained $\mu_{3D} = 170 \pm 20$ cm$^2$/Vs at a high carrier concentration of $2.1 \times 10^{10}$ cm$^{-3}$ where charge carriers are optically injected via interband absorption which differs from traditional doping of bulk samples. A larger mobility leads to higher electrical conductivity in the degenerate case; thus, $\mu_{3D} = 170$ cm$^2$/Vs is taken as the upper limit at room temperature to calculate $\sigma_{3D}$ in the similar range of carrier concentrations estimated from Eq. (9). In the degenerate limit, $\sigma_{3D}$ (= $n\mu_{3D}$) is calculated to be about 250% higher than $\sigma_{BL}$, as shown in Fig. 2(b). This is due to more effective doping (the Fermi level is expected to move into the parabolic band at lower carrier concentrations) in the non-discretized DOS, resulting in easier accessibility of the band states in 3D over bilayer MoS$_2$. It is important to note that these electrical conductivity values for 3D MoS$_2$ are based on the upper limit of mobility ($\mu_{3D} = 170$ cm$^2$/Vs) in this model which will be further discussed later.

Subsequently, considering the energy-independent 2D DOS and all possible scattering parameters, the Seebeck coefficient for all 3D and 2D MoS$_2$ samples is calculated using the steady-state solution to the linearized BTE in Eq. (2). In Fig. 3, the experimental Seebeck coefficients for monolayer and bilayer MoS$_2$ are fitted with the BTE model of all monolayer, bilayer, and 3D MoS$_2$ samples ($S_{ML}$, $S_{BL}$, and $S_{3D}$) for acoustic phonon as well as intervalley scattering with $r = 0$ and $r = -1/2$ for 2D and 3D, respectively (see Table I for details).

The Seebeck coefficients are negative, indicating n-type conduction carriers (electrons), and are inversely proportional to carrier concentration. Hence, the Seebeck coefficients decrease as the carrier concentration ($n$) is increased as shown in Fig. 3. Here, $S_{BL}$ is larger than $S_{3D}$ owing to quantum confinement, which allows for a larger asymmetry of the DOS around the Fermi level in the degenerate limit compared to the 3D case. This asymmetry of the DOS at the CBM is in turn controlled by the broadening of the window function, $F_{w}(E,T)$. The window function is odd around $E = E_F$, producing a local maxima and minima where the Seebeck coefficient is expected to be large. The experimental Seebeck coefficient for 2D MoS$_2$ ($S_{ML, ex}$ and $S_{BL, ex}$) agrees reasonably well with the acoustic phonon and/or intervalley scattering ($r = 0$) BTE model in Fig. 3 and further validates the estimation of a constant relaxation time obtained from the electrical conductivity data in Fig. 2(b). The 2D MoS$_2$ samples can have sulfur vacancies and charged impurities from the underlying substrate,\textsuperscript{28,41} as well as ripples,\textsuperscript{42} thus introducing additional disorder into the system. Hence, the experimental monolayer MoS$_2$ is not degenerately doped due to impurity states in addition to the band DOS, and thus, Eq. (2) does not give an exact fit to the experimental data. The bilayer sample is presumably cleaner and/or less sensitive to scattering from the underlying SiO$_2$, and hence, the theoretical curve fits the data better. Using the same BTE model, if charged impurity scattering ($r = 3/2$) is dominant in 3D MoS$_2$, its Seebeck coefficient will be enhanced which will be discussed in Sec. IV.

Consolidating the results above, the thermoelectric powerfactor ($S^2\sigma$) can then be calculated. In the degenerate limit, the power factor exhibits a peak at an optimal carrier concentration ($n_{opt}$).\textsuperscript{17} The power factor for all MoS$_2$ samples is plotted, each exhibiting a peak at $n_{opt}$ which corresponds to the optimal Seebeck coefficient of each sample indicated as arrows in Fig. 4. The optimal powerfactor exhibited by 2D and 3D MoS$_2$ samples is $S^2\sigma_{ML, opt} = 2.00$ mW/m$^2$ K, $S^2\sigma_{BL, opt} = 12.01$ mW/m$^2$ K, and $S^2\sigma_{3D, opt} = 6.22$ mW/m$^2$ K, respectively. Next, the optimal Seebeck coefficient ($S_{opt}$) from $n_{opt}$ of the MoS$_2$ Samples is extrapolated, revealing a higher Seebeck coefficient in 2D bilayer MoS$_2$ ($S_{BL, opt} = -165.7$ $\mu$V/K) over the 2D monolayer ($S_{ML, opt} = 160.9$ $\mu$V/K) and 3D MoS$_2$ ($S_{3D, opt} = -132.1$ $\mu$V/K). It is also important to note that the optimal Seebeck coefficients of all MoS$_2$ samples fall in the window function of $\sim 2$kT, where the maximum Seebeck coefficient is expected to occur.

### IV. DISCUSSION

Interestingly, although the bilayer MoS$_2$ is predicted to exhibit a superior Seebeck coefficient over 3D and monolayer MoS$_2$, the electrical conductivity of 3D MoS$_2$, $\sigma_{3D}$ calculated using $\mu_{3D} = 170$ cm$^2$/Vs is 250% higher than $\sigma_{BL}$. However, under acoustic phonon-limited scattering (acoustic phonons and intervalley scattering), our 3D carrier concentration ($\sim 1.3 \times 10^{20}$ cm$^{-3}$) is about one order of magnitude higher than that observed by Kumar et al. ($2.1 \times 10^{19}$ cm$^{-3}$).\textsuperscript{40} Since a larger carrier concentration translates to a higher scattering probability and thus a further reduced mobility, we expect the acoustic phonon-limited (AP) scattering mobility, $\mu_{3D-AP}$ to

![FIG. 3. Theoretical Seebeck coefficient fitted as a function of carrier concentration with scattering parameter $r = 0$ for all MoS$_2$ samples. The Seebeck coefficient for both 2D MoS$_2$ samples fits the acoustic phonon scattering model reasonably well with slight deviation, confirming that acoustic phonon scattering is dominant in 2D MoS$_2$ at 300 K. The slight deviation from $r = 0$ is possibly due to contributions from other scattering mechanisms, and the impurities in our exfoliated MoS$_2$ samples.

be lower than the upper limit of 170 cm$^2$/Vs used in this model.

Under the charged impurity scattering regime, another point to be noted is that for 3D semiconductors (e.g., Silicon, GaAs) with such high levels of doping, scattering is typically dominated by charged impurities.\textsuperscript{23,24} For example, n-doped Silicon with an effective mass of 0.1 $m_0$ (and a 6-fold valley degeneracy) has mobilities around 50 to 100 cm$^2$/Vs at doping levels of $\sim 10^{20}$ cm$^{-3}$.\textsuperscript{23,38} Taking a step back, referring to the calculations by Fivaz and Mooser with homopolar optical phonons (HOP) being the dominant scattering mechanism,\textsuperscript{39} the mobility of $\mu$\textsubscript{HOP} $\sim 100$ cm$^2$/Vs is estimated at a much lower carrier concentration ($\sim 10^{16}$ cm$^{-3}$). If charged impurity (CI) scattering were to become dominant at carrier concentrations of $\sim 10^{20}$ cm$^{-3}$, then $\mu$\textsubscript{HOP} must be lower than both $\mu$\textsubscript{AP} and $\mu$\textsubscript{HOP}. Despite the aforementioned enhancement in the Seebeck coefficient, the bilayer MoS$_2$ remains superior over 3D MoS$_2$ due to the unfavourable $\mu$\textsubscript{CI}. Therefore, taking $\mu$\textsubscript{3D} = 170 cm$^2$/Vs as the upper limit is a safe estimate for 3D MoS$_2$ in our acoustic phonon-limited scattering model and hopefully future experiments on highly doped bulk MoS$_2$ will serve to validate this limit.

Analyzing the powerfactor of all MoS$_2$ samples ($S^2\sigma_{\text{ML, opt}} = 2.00$ mW/m$^2$K, $S^2\sigma_{\text{BL, opt}} = 12.01$ mW/m$^2$K, and $S^2\sigma_{3D, opt} = 6.22$ mW/m$^2$K), the bilayer MoS$_2$ is superior over 3D and monolayer MoS$_2$, with a 200% and 600% enhancement in thermoelectric performance, respectively, arising directly from a larger Seebeck coefficient and an experimentally verified acoustic phonon-limited mobility. However, a direct comparison between our 2D MoS$_2$ samples and projected 3D MoS$_2$ values at similar doping levels is still rudimentary and lacks experimental investigation of the powerfactor in doped 3D MoS$_2$ samples.

Overall, the experimental powerfactor for 2D MoS$_2$ samples fits very well with our calculations therefore capturing the physics of scattering and the discretization of the density of states effectively. The valley degeneracy and mobility of the bilayer MoS$_2$ are 3 and 2 times higher than those of the monolayer MoS$_2$, respectively, accounting for the 600% difference in their respective optimal electrical conductivity ($\sigma_{\text{opt}}$) and hence in powerfactor ($S^2\sigma_{\text{opt}}$). This means that the effectiveness of quantum confinement is similar in monolayer and bilayer MoS$_2$ and the difference in their thermoelectric performance is simply due to a difference in the bandstructure. In this study, we showed that the powerfactor is maximized at an optimal doping concentration, and that dimensionality confinement enhances the Seebeck coefficient in 2D over 3D MoS$_2$ under acoustic phonon-limited scattering. If charged impurity scattering is considered for 3D MoS$_2$, the thermoelectric powerfactor of 2D bilayer MoS$_2$ is expected to be still better than that of 3D MoS$_2$ due to a reduced mobility ($\mu$\textsubscript{3D, CI} < $\mu$\textsubscript{3D, AP}), in agreement with theoretical studies of Dresselhaus.\textsuperscript{4} Kim et al. concluded that in a 2D material, the powerfactor per mode is $\sim 70\%$ larger than in a 3D material, assuming ballistic conductors where scattering is not taken into consideration.\textsuperscript{10} The electrical conductivity and thermoelectric powerfactor of bilayer MoS$_2$ were recently observed to be higher than those of monolayer MoS$_2$ similar to our study, but not compared with 3D MoS$_2$.\textsuperscript{18} In addition, we explicitly consider the change in the bandstructure between monolayer and bilayer MoS$_2$ which verifies why the bilayer MoS$_2$ is superior. In our acoustic phonon-limited scattering model, $S^2\sigma_{\text{BL}}$ is 200% larger than $S^2\sigma_{3D}$. Under charged impurity scattering, with both mobility and electrical conductivity reduced, $S^2\sigma_{\text{BL}}$ will still remain larger than $S^2\sigma_{3D}$. The thermoelectric performance of 3D MoS$_2$ over 2D MoS$_2$ remains to be verified due to the lack of experimental investigation into 3D MoS$_2$ under similar doping concentrations.

Comparing against other TMDC materials such as MoSe$_2$/WSe$_2$, considering their Seebeck coefficient based solely on their effective mass and degeneracies\textsuperscript{43} with the same assumption that acoustic phonon scattering is dominant, we can therefore predict that MoSe$_2$ is capable of a high thermoelectric powerfactor as well. Nanostructuring and alloying of these layered compounds can be employed to reduce the thermal conductivity while taking advantage of the high powerfactor to make a feasible thermoelectric material and is an exciting avenue for future research.

![FIG. 4. Calculation results for thermoelectric powerfactor ($S\sigma$) vs carrier concentration of all 2D (monolayer and bilayer) and 3D MoS$_2$ samples. The optimal powerfactor for each sample occurs at the optimal $n_{\text{opt}}$ represented by the arrows, respectively, where each optimal electrical conductivity ($\sigma_{\text{opt}}$) and Seebeck coefficient ($S_{\text{opt}}$) can be extracted.](image-url)
ACKNOWLEDGMENTS

We acknowledge financial support from the A*Star Science and Engineering Research Council (Grant No. 152 70 00015). The authors thank J. Wu for his assistance with Fig. 1.

1G. J. Snyder and E. S. Toberer, Nat. Mater. 7, 105 (2008).
17D. M. Rowe, Handbook of Thermoelectrics (CRC Press, 1995).
44N. Kumar, J. He, D. He, Y. Wang, and H. Zhao, J. Appl. Phys. 113, 133702 (2013).