

Effects of alloying on in-plane thermal conductivity and thermal boundary conductance in transition metal dichalcogenide monolayers

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Two-dimensional 1H transition metal dichalcogenides (TMDs) provide a platform, analogous to group IV cubic semiconductor alloys (Si_{1-x}Ge), that enables systematic investigations on the effects of alloying in 2D material systems. The existing literature on TMD alloys explores their electrical, magnetic, and optical properties, but lacks a comprehensive analysis of thermal transport in supported and nanostructured systems. Here we employ first-principles-driven phonon Boltzmann transport formalism and a 2D-3D thermal boundary conductance model to systematically study in-plane and cross-plane phonon transport of suspended and SiO_2 supported single-layer TMD alloys. We find that the thermal conductivity of alloyed TMDs is dependent on system size up to tens of microns and that the combination of mass-difference and substrate scattering can significantly reduce thermal transport even in large systems (>500 nm). Beyond in-plane transport, we find that the thermal boundary conductance displays a qualitatively different trend and significantly weaker modulation with alloy composition as compared to the thermal conductivity. Our results help shed light on the in-plane and cross-plane thermal transport properties of 2D single-layer TMD alloys and further their applications in nanoelectronics, sensing, and energy devices.

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I. INTRODUCTION

Inherently semiconducting two-dimensional (2D) materials are essential for all-2D electronic and optoelectronic devices. Single-layer transition metal dichalcogenides (TMD) are a family of semiconducting materials with a range of band gaps and electron/hole mobilities, making them a model semiconductor family for 2D transistors and photonics. Beyond homogeneous TMDs, great attention has been given to the electronic, magnetic, and optical properties of TMD alloys, which have been readily synthesized through chemical vapor transport (CVT), chemical vapor deposition (CVD), and physical vapor deposition (PVD) [1–3]. Furthermore, the scalability, thickness-controlled exfoliation, and thermal stability of a wide range of quasibinary TMD alloys was recently demonstrated [3]. Thermal transport in few- and single-layer homogeneous 2D materials has been investigated at length [4–13]. However, despite their potential applications in solid-state memory, optoelectronics, and thermoelectric (TE) devices [14–16], there has been less attention given to the thermal properties of TMD alloys.

Alloying is a method for tuning vibrational frequencies, reducing the lattice thermal conductivity, and tuning the bandgap while having only moderate impact on electrical conductivity relative to the strong impact seen on phonon transport. It is therefore a commonly employed method for improving the conversion efficiency of TEs, which requires high electrical and low thermal conductivity. Considering that the modest thermal conductivity in sub-micron scale

homogeneous TMDs has spurred interest in employing them in TEs [17–22], TMD alloys could stand to drive interest further. Composition- and temperature-dependent in-plane thermal conductivity (κ_{IP}) was measured in bulk quasibinary $\text{WSe}_{2-2x}\text{Te}_{2x}$ alloys by time-domain thermoreflectance where a three- to fourfold reduction in κ_{IP} was reported in the alloyed samples as compared to the homogeneous counterparts [23]. Janus TMDs are compounds that have one of the chalcogen layers replaced by a different chalcogen element (such as in a S-Mo-Se trilayer) [24,25]. The effect of such replacement on the thermal conductivity appears to be linear [26], which contrasts with the highly nonlinear effects observed in alloys with randomized constituent positions [15,27].

Due to the computational costs of density-functional perturbation theory and frozen-phonon methods, computing full phonon dispersions of randomized alloys remains a challenge due to the large supercells required, especially for dilute alloy compositions. Consequently, much of the *ab initio* approaches on TMD alloys focus on simpler structures, such as Janus compounds [25,26], or more computationally tractable quantities, such as ground state energies and electronic band structures [28–30]. Such impediments can be alleviated by molecular dynamics [27] which can handle larger simulation sizes and, perhaps more effectively, by employing the *virtual crystal approximation* (VCA) within an *ab initio* framework. The VCA typically takes advantage of first-principles full-phonon dispersions of the homogeneous materials and linearly interpolates the lattice constants, atomic masses, and harmonic force constants of the constituents to replace the homogeneous unit cell observables with virtual approximations [31]. Combined with an alloy-scattering rate that captures the effects of mass disorder on phonon scattering, the VCA

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has been demonstrated to accurately capture the dispersion of acoustic phonons [32] and be a powerful tool for examining thermal conductivity in binary semiconductor alloys [33].

To this end, the VCA has previously been employed with a Green's function approach to alloy scattering where the thermal conductivity was solved via a first-principles-driven Boltzmann transport equation (DFT-BTE) [15]. There the authors reported a sixfold reduction in the room-temperature thermal conductivity of single-layer $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ alloys as a function of W concentration. The effects of nanodomains ranging from ~ 2 –11 unit cells in size were examined where a moderate (40%) domain-size-independent reduction in the thermal conductivity was observed. Despite the aforementioned studies, the literature is lacking comprehensive analysis on length dependence and effects of nanostructuring on thermal transport in TMD alloys. Moreover, there is no literature on the effects of substrate scattering on the in-plane thermal conductivity or on cross-plane thermal conductance from TMD alloys into the substrate, which is the key heat-removal pathway in 2D devices [34].

In this work, we study the effects of alloy composition on both in-plane (thermal conductivity) and through-plane (2D-3D thermal boundary conductance) thermal transport in 1H MX_2 TMD quasibinary alloys, i.e., $\text{M}_{1-x}\text{M}'_x\text{X}_2$ and $\text{MX}_{2-2x}\text{X}'_{2x}$ where $\text{M}, \text{M}' = \text{Mo}, \text{W}$ and $\text{X}, \text{X}' = \text{S}, \text{Se}$. We use first-principles calculations of the phonon dispersions of 1H homogeneous MoS_2 , MoSe_2 , WS_2 , and WSe_2 and then compute the alloyed parameters within the VCA. We employ a phonon Boltzmann transport model for in-plane transport [35] and a cross-dimensional (2D-3D) thermal boundary conductance model [36] for through-plane transport. We report a near order of magnitude (three- to fivefold) reduction in the room temperature κ_{IP} as a function of alloy composition for $5 \times 5 \mu\text{m}^2$ systems. We further show that κ_{IP} is reduced significantly in both homogeneous and alloyed TMDs through nanostructuring, which introduces line-edge roughness scattering, and substrate scattering when the TMDs are placed atop SiO_2 . Beyond in-plane conductivity, we provide novel insight into alloy effects on thermal transport from the 2D layer into the underlying substrate and comment on the thermal healing length as a function of alloy composition in TMD alloys. We demonstrate a robust modulation in the thermal conductivity of bulk and nanostructured TMD alloys which could immediately benefit the design of TMD-based devices.

The remainder of this paper proceeds as follows: Section II discusses the first-principle phonon dispersions and transport models for in-plane thermal conductivity and thermal boundary conductance. Note that we refer to the Appendix for details on first-principles calculations, and anharmonic, edge-roughness, and substrate scattering rates to supplement the methodology. Section III discusses the results of alloying mixing on thermal conductivity, thermal boundary conductance, and thermal healing length.

II. METHODOLOGY

A. Phonon dispersions from first principles and VCA

We calculate the full-phonon dispersion of four homogeneous transition metal dichalcogenide monolayers (MoS_2 ,

MoSe_2 , WS_2 , and WSe_2) using density-functional perturbation theory (DFPT) as implemented within the PHonon package as distributed with the open-source package QUANTUM ESPRESSO [37,38]. The calculated full-phonon dispersion relations of MoS_2 , WS_2 , MoSe_2 , and WSe_2 are shown in Figs. 1(a)–1(d). The mode-dependent phonon group velocities v_g and Grüneisen parameters γ are then calculated from the dispersion data using a central difference method applied to

$$v_g(Q) = \frac{\partial \omega(Q)}{\partial \mathbf{q}} \quad (1)$$

$$\gamma(Q) = -\frac{a_0}{2\omega(Q)} \frac{\partial \omega(Q)}{\partial a}, \quad (2)$$

where Q represents the reduced phonon mode $(\mathbf{q}, j)$ for wave-vector $\mathbf{q}$ and branch j . In the case of the Grüneisen parameters, the monolayer is biaxially strained by a small (± 0.5) percentage and the chalcogen-chalcogen distance is adjusted in a structural optimization step that maintains a constant in-plane lattice constant.

After we obtain the phonon dispersion and related quantities of each TMD, we then approximate quasibinary alloys—mixing either the transition metals or chalcogens—using the *virtual crystal approximation* (VCA). In implementing the VCA, we linearly mix the square of the phonon dispersions, lattice constants, and atomic masses of the constituent materials [39,40]. The phonon dispersion of an $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ alloy is shown in Fig. 1(e). Once we have the VCA alloy dispersions, we then input them into our phonon Boltzmann transport (pBTE) model for in-plane transport or into our 2D-3D interface model to study the thermal boundary conductance between these materials and an amorphous SiO_2 substrate.

We also consider the effect of substrate coupling on the vibrational modes of the 2D layer. When a 2D layer is placed on a substrate, flexural phonons that characteristically displace atoms vertically, normal to the interface, experience a restoring force in the long-wavelength regime caused by the collective forces of the van der Waals (vdW) bonds governing interface coupling [36]. As a result, 2D layers supported by substrates see a resonant peak in the flexural (ZA) phonon branch in the long-wavelength regime that is representative of the restoring forces of substrate coupling. The resonant frequency ω_0 is determined from the vdW coupling spring constant (K_a), the number of atoms per unit cell with a vdW bond to the substrate N , and the unit cell mass m of the 2D material— $\omega_0 = \sqrt{NK_a/m_{2D}}$. The inset of Fig. 1(e) shows the gapped ZA branch in red $\tilde{\omega}_{\text{ZA}}(\mathbf{q}) = \sqrt{\omega_{\text{ZA}}^2(\mathbf{q}) + \omega_0^2}$ and the as-calculated ungapped branch $\omega_{\text{ZA}}(\mathbf{q})$ in dashed gray.

B. In-plane phonon BTE and mass-difference scattering

The phonon Boltzmann transport equation (pBTE) has been widely used to study thermal transport in semiconductor materials [41,42] as well as two-dimensional graphene [35]. Here we use an Allen-Callaway (AC) solution [43] to the pBTE, which accounts for the additional thermal conductivity from the flowing equilibrium governed by nonresistive normal phonon scattering processes [44]. The steady-state pBTE is

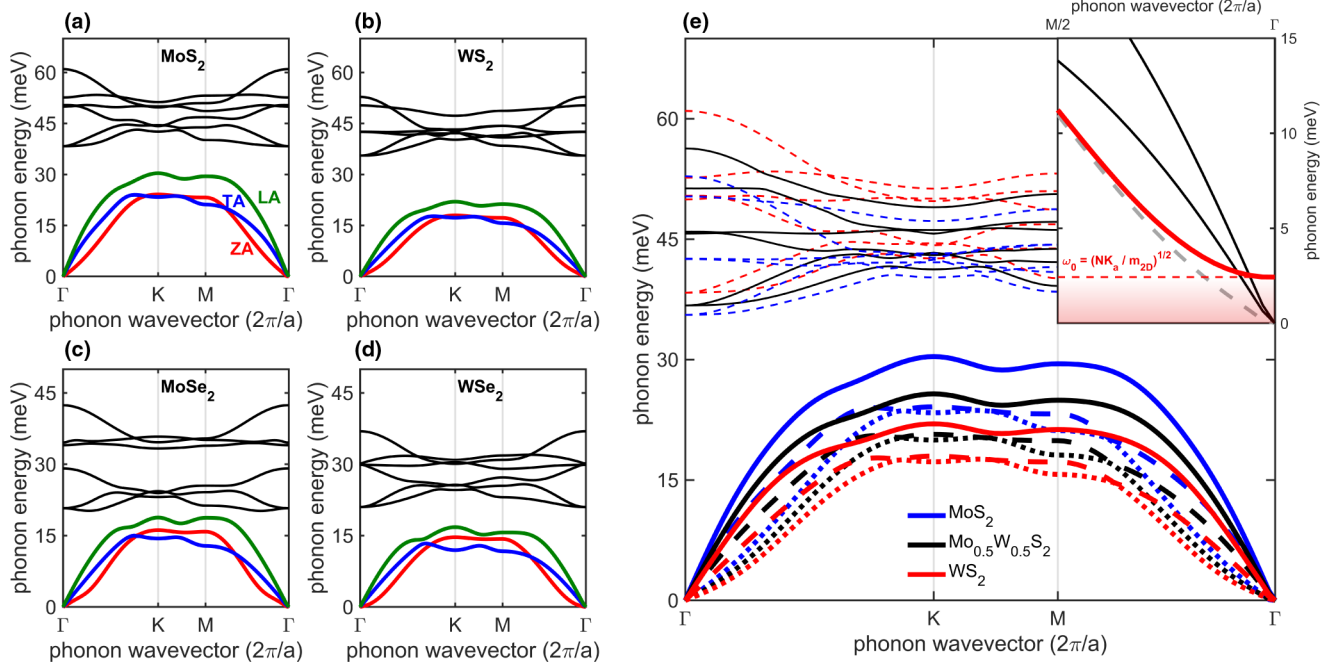


FIG. 1. The phonon dispersion of (a) MoS₂, (b) WS₂, (c) MoSe₂, and (d) WSe₂ obtained from first-principles DFPT simulations. In (e) we show the first-principles calculated phonon dispersion of MoS₂ (dashed red line) and WS₂ (dashed blue line) as well as the resulting dispersion from a VCA of a 50/50 alloy between the transition metals Mo and W (solid black line). The inset of (e) illustrates the gapping that the out-of-plane, flexural phonon branch undergoes when the 2D layer is placed on a substrate.

written as

$$\vec{v}_Q \cdot \nabla_{\vec{r}} N_Q = -\frac{N_Q - N_Q^0}{\tau_Q^R} - \frac{N_Q - N_Q^*}{\tau_Q^N}, \quad (3)$$

where on the left hand side $\vec{v}_Q$ is the phonon velocity and $\nabla_{\vec{r}} N_Q$ is the spatial gradient of the out-of-equilibrium distribution function N_Q , while on the right hand side, $1/\tau_Q^R$ represents the resistive scattering rate which relaxes the out-of-equilibrium distribution N_Q back to a zero heat flux equilibrium distribution N_Q^0 , represented by the Bose-Einstein distribution function $N_Q^0(T) = [\exp(\hbar\omega_Q/k_B T) - 1]^{-1}$. Further, $1/\tau_Q^N$ represents the nonresistive (normal) scattering rate that pushes the out-of-equilibrium distribution toward a nonzero heat flux flowing equilibrium distribution N_Q^* .

Within the AC solution the total thermal conductivity κ can be written conveniently as a sum,

$$\kappa = \kappa_{\text{RTA}} + \frac{\lambda_1 \lambda_2}{\lambda_3}, \quad (4)$$

which consists of the widely used relaxation time approximation (RTA) term κ_{RTA} plus a correction term $\frac{\lambda_1 \lambda_2}{\lambda_3}$. The RTA term is written as

$$\kappa_{\text{RTA}}(T) = \frac{k_B}{h_{2D}} \sum_{j,q} \hbar\omega_Q \frac{\partial N_Q^0}{\partial T} \tau_Q^C v_Q^2, \quad (5)$$

where k_B is Boltzmann's constant, h_{2D} is the 2D layer thickness (including interplanar vdW gap) [45], $\hbar\omega_Q$ represents phonon energy, $\frac{\partial N_Q^0}{\partial T}$ is the temperature derivative of the equilibrium Bose-Einstein distribution function, τ_Q^C is the total

relaxation time, and v_Q represents the phonon group velocity. In Allen's solution $\lambda_{1,2,3}$ are written in the following form

$$\lambda_1 = \frac{1}{A\delta} \sum_Q v_{Q\parallel} Q_{\parallel} \tau_Q^C \frac{\partial N_Q^0}{\partial T}, \quad (6)$$

$$\lambda_2 = \frac{1}{A\delta} \sum_Q v_{Q\parallel} Q_{\parallel} \left[\frac{\tau_Q^C}{\tau_Q^N} \right] \frac{\partial N_Q^0}{\partial T}, \quad (7)$$

$$\lambda_3 = \frac{1}{A\delta} \sum_Q \left(\frac{Q_{\parallel}^2}{\hbar\omega_Q} \right) \left[\frac{\tau_Q^C}{\tau_Q^R} \right] \frac{\partial N_Q^0}{\partial T}, \quad (8)$$

where $Q_{\parallel}$ is the component of the phonon wave vector that is perpendicular to the boundary normal and parallel to the temperature gradient. Collectively, $\lambda_{1,2,3}$ quantify the additional thermal conductivity produced by the flowing equilibrium. In Eqs. (5)–(8), τ_Q^C combines all resistive τ_Q^R and nonresistive τ_Q^N scattering mechanisms, that is $1/\tau_Q^C = 1/\tau_Q^R + 1/\tau_Q^N$.

Resistive scattering mechanisms are comprised of any collision that destroys crystal momentum, which includes anharmonic Umklapp scattering $1/\tau_Q^U$, isotope scattering $1/\tau_Q^{\text{iso}}$, impurity scattering $1/\tau_Q^{\text{imp}}$, alloy mass-difference scattering $1/\tau_Q^{\text{mass}}$, line-edge roughness scattering $1/\tau_Q^{\text{LER}}$, and substrate scattering $1/\tau_Q^{\text{sub}}$. The scattering rate of resistive processes is thus written as

$$\frac{1}{\tau_Q^R} = \frac{1}{\tau_Q^U} + \frac{1}{\tau_Q^{\text{mass}}} + \frac{1}{\tau_Q^{\text{imp}}} \dots \\ \dots + \frac{1}{\tau_Q^{\text{iso}}} + \frac{1}{\tau_Q^{\text{LER}}} + \frac{1}{\tau_Q^{\text{sub}}}. \quad (9)$$

In this work we are interested in TMD alloys where mass-difference scattering $1/\tau_Q^{\text{mass}}$ caused by the random mixing of atomic species dominates in contribution to $1/\tau_Q^R$. For sake of brevity, we discuss the anharmonic three-phonon (normal $1/\tau_Q^N$ and Umklapp $1/\tau_Q^U$), line-edge roughness $1/\tau_Q^{\text{LER}}$, and substrate scattering rate $1/\tau_Q^{\text{sub}}$ in the Appendices 2 and 3, respectively.

Phonon scattering from mass disorder is primarily due to alloying but can similarly occur with mass variation from isotopes and vacancies/impurities. These mechanisms are elastic and can be written in terms of the phonon density of states as [42,46,47]

$$\frac{1}{\tau_{\text{mass}}(\omega)} = \frac{\pi S_0}{12} \Gamma_0 \omega^2 D_{2D}(\omega), \quad (10)$$

where S_0 is the unit cell surface area and Γ_0 is the mass-difference scattering constant, which is related to the likelihood of encountering a mass-different body and the resulting mass perturbation. When the material is alloyed Γ_0 takes the following form

$$\Gamma_0 = \frac{x(1-x)(m_1 - m_2)^2}{m_{\text{alloy}}^2}. \quad (11)$$

In the above, m_{alloy} represents a linear mixing of the unit cell masses of the homogeneous TMDs, as in $m_{\text{alloy}} = (1-x)m_1 + xm_2$. The phonon density of states $D_{2D}(\omega)$ is calculated following the Brillouin zone integration method [48], which for dense q -point grids can be numerically calculated as a sum over all phonon modes $Q = (\mathbf{q}, j)$, $D_{2D}(\omega) = \sum_Q \delta[\omega - \omega_Q]$. Equation (10) is derived from perturbation theory wherein a dot product between incident and final phonon displacement vectors occurs [46]. In 2D materials, this dot product restricts the scattering channels between ZA and TA/LA phonons because their displacement vectors are always perpendicular [49], which is an instance of a more general selection rule that requires scattering processes in inversion-symmetric 2D materials to always involve an even number of ZA phonons [45]. Therefore, elastic mass-difference scattering events involving ZA phonons must result in a ZA phonon [$D_{2D} \rightarrow D_{ZA}$ in Eq. (10)], whereas events involving TA/LA phonons can result in any phonon except ZA [$D_{2D} \rightarrow D_{\text{TA/LA}}$ in Eq. (10)].

Alloy scattering is typically stronger than isotope or impurity scattering due to the larger mass difference ($m_1 - m_2$) between the constituent materials even at small mixing percentages [42,50]. For phonon collisions with isotopes, Γ_0 represents the natural abundance of isotopes and can be written as $\Gamma_0 = \chi(1-\chi)/(\bar{M} + \chi)^2$ with $\chi = 3.4\%$. Scattering with impurities occurs with lattice vacancies/defects and has a $\Gamma_0 = S_0 n_{\text{imp}}$ where n_{imp} is the concentration of impurities. Under controlled conditions, impurity concentrations are typically fractions of a percent of the atomic density of the host material (on the order of $3-4 \times 10^{15} \text{ cm}^{-2}$ in TMDs). High-purity few-layered TMDs are reported [51,52] to have impurity concentrations on the order of 10^{10} – 10^{11} cm^{-2} . At these amounts the impact on thermal conductivity is minimal (~ 5 – 15% on the large system κ_{IP} and ~ 1 – 3% in alloys). Hence we neglect impurity scattering in our calculations for alloys by assuming their concentrations to be negligible.

C. 2D-3D thermal boundary conductance

In calculating the thermal boundary conductance (TBC) between the 2D layer and its underlying substrate we employ our previously developed cross-dimensional 2D-3D thermal boundary conductance model [36,53]. This model has been demonstrated to quantitatively reproduce the temperature-dependent TBC of graphene-SiO₂, MoS₂-SiO₂, AlO_x-MXene-SiO₂, and FL-WSe₂-SiO₂ interfaces [36,53–55]. Contrary to 3D-3D interfaces where phonons impinge on the interface to undergo a transmission or reflection process, phonons propagating in the 2D layer travel parallel to the 2D-3D interface. Consequently, under traditional thermal interface models, such as the diffuse and acoustic mismatch models [56,57] (DMM and AMM) or the more recent vdW-AMM [58], 2D-3D TBC would be zero [36]. In 2D-3D interface systems, phonons propagating in the plane of the 2D layer undergo an additional scattering process due to coupling of out-of-plane displacements with vibrations in the substrate through the vdW bonds. In those substrate scattering events, a phonon may hop across the interface thereby contributing the interface transport. Hence, in this context, scattering of phonons in the monolayer facilitates interface transport as opposed to hindering it for in-plane transport.

As a result of the above, 2D-3D thermal boundary conductance is uniquely bottlenecked by two mechanisms: (i) out-of-plane ZA phonons that displace atoms vertically are the primary carriers of thermal energy across the interface [59]; therefore, the thermal channel from 2D to 3D systems must go through ZA phonon interactions, and (ii) when ZA phonons transfer across the interface the ZA phonon population in the 2D layer is diminished. This depletion of the ZA phonon population is replenished by the collective internal scattering of ZA phonons, which consists of three-phonon anharmonic (normal and Umklapp) and line edge roughness scattering; $1/\tau_{\text{int}} = 1/\tau_N + 1/\tau_U + 1/\tau_{\text{LER}}$. We denote any additional resistance brought on by the slow repopulation of ZA phonons in the 2D layer as the *internal resistance* (R_{int}). Further, we point out that the internal conductance ($G_{\text{int}} = R_{\text{int}}^{-1}$) can be qualitatively thought of as one part of a series conductor network with the external conductance—termed *external TBC*—which is determined strictly by the substrate scattering rate $1/\tau_{\text{sub}}$ (i.e., in the limit of very large internal scattering).

The rate at which phonons transfer across the 2D-3D interface is obtained from Fermi's golden rule as [59]

$$\frac{1}{\tau_{\text{sub}}(\omega)} = \frac{\pi}{2} \frac{D_{\text{sub}}(\omega)}{m_{\text{sub}} m_{\text{alloy}}} \frac{N K_a^2}{\omega^2}. \quad (12)$$

Here, the m_{alloy} is the unit cell mass of the TMD alloy, K_a is the vdW coupling spring constant, and N is the number of atoms with vdW springs in the 2D unit cell. The vibrational density of states (vDOS) of amorphous SiO₂ is extracted from previous molecular dynamics simulations [60]. Once we calculate the substrate scattering rate, internal ZA scattering rates, and the vDOS of the 2D layer, we calculate the TBC as the product of the specific heat and vDOS of the 2D layer and effective substrate scattering rate integrated over all phonon energies

$$G(T) = \int C_{2D}(\omega, T) D_{2D}(\omega) \tau_{\text{eff}}^{-1}(\omega) d\omega, \quad (13)$$

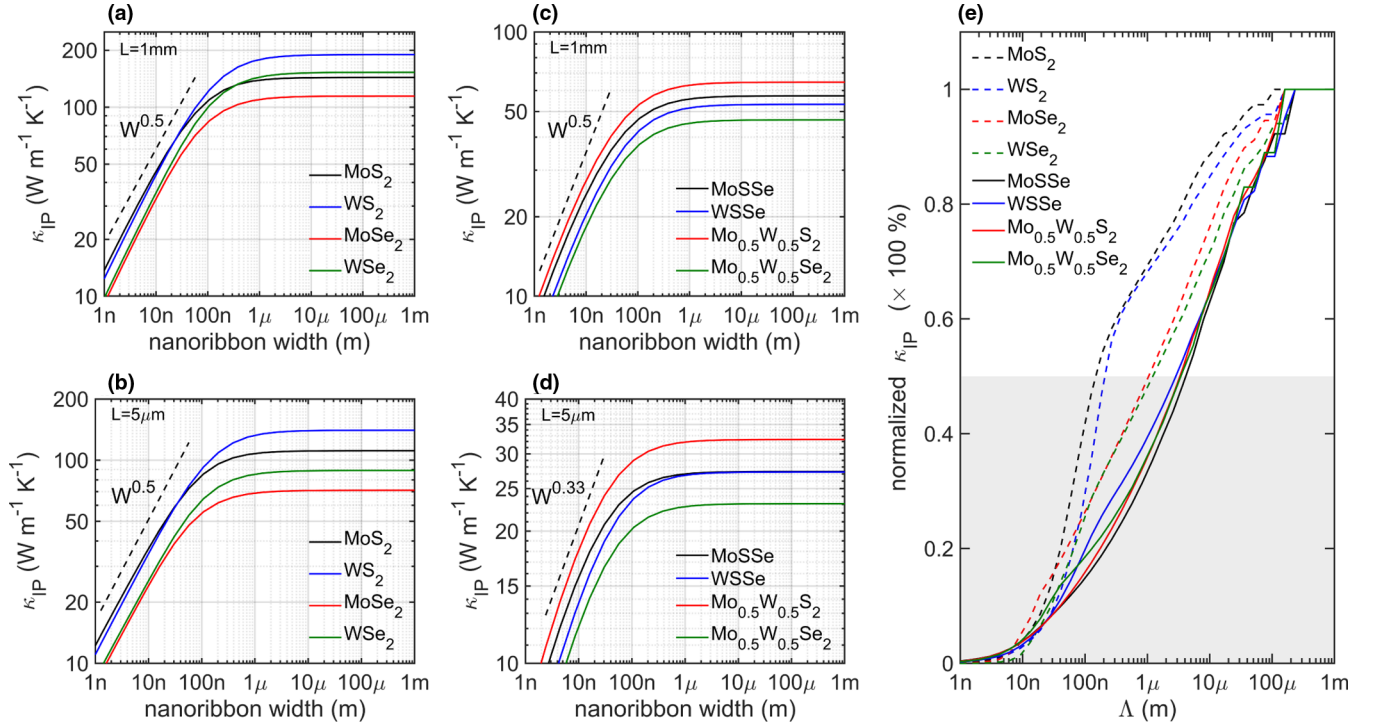


FIG. 2. The width dependence of $L = 1$ mm and $L = 5$ μ m long (a),(b) homogeneous and (c),(d) 50% alloyed nanoribbon TMD systems. The cumulative thermal conductivity as a function of phonon mean-free-path Λ is shown in (e). We use an rms edge roughness $\Delta = 0.45$ nm for all calculations.

where

$$\tau_{\text{eff}} = \tau_{\text{sub}} + \tau_{\text{int}}. \quad (14)$$

Here we can anticipate that the modulation of unit cell mass, phonon density of states of the 2D layer, and Grüneisen parameter γ (as $\tau_{\text{int}} \propto \gamma^2$) through alloy mixing will lead to a nontrivial influence on the TBC as compared to the well-known trends commonly obtained for thermal conductivity.

III. RESULTS AND DISCUSSION

A. Size dependence of in-plane thermal conductivity

Previous reports of κ_{IP} for homogeneous TMDs with system dimensions in the 1–10 micron range give values of 120–140, 80–100, 72, and 46.2 W m⁻¹ K⁻¹ for WS₂, MoS₂, WSe₂, and MoSe₂, respectively [6,9,12,13]. Our calculations of room temperature κ_{IP} in suspended single-layer homogeneous and 50% alloyed TMDs over several orders-of-magnitude of width (W) at two lengths ($L = 1$ mm and $L = 5$ μ m) are shown in Figs. 2(a)–2(d). For large homogeneous ($L = 1$ mm, $W > 1$ μ m) systems, we obtain in-plane conductivity values of 143.7, 190, 153, and 114.5 W m⁻¹ K⁻¹ for MoS₂, WS₂, WSe₂, and MoSe₂, respectively. The *bulk* values in previous reports are of systems with size dimensions in the 1–10 micron range and may still be partly limited by boundary scattering if large mean-free-path (MFP) phonons ($\Lambda > L$) are non-negligible. When we reduce L to the micron range ($L = 5$ μ m), we find good agreement between our large-width $W > 1$ μ m [Fig. 2(b)] homogeneous calculations and previous DFT-BTE predictions with values of 140.4,

111.3, 89, and 71 W m⁻¹ K⁻¹ for WS₂, MoS₂, WSe₂, and MoSe₂, respectively.

Comparing the $L = 1$ mm large-width 50% alloyed TMD alloys [Fig. 2(c)] with the homogeneous TMDs, we see a factor of 2–3 reduction in κ_{IP} . Despite strong alloy scattering [Eq. (10)], the large alloy systems maintain moderate thermal conductivity values around 46–65 W m⁻¹ K⁻¹. As width dimensions are scaled down below the ~ 1 μ m range in the homogeneous TMDs (100 nm in the alloys), we begin to see a significant reduction in κ_{IP} due to phonon collisions with rough edges. Interestingly, we find the width dependence below 100 nm follows a $\kappa_{IP} \propto W^{1/2}$ trend, which has been observed for in-plane and cross-plane thermal conductivity in 3D thin films and attributed to the quadratic dependence of anharmonic scattering rates on frequency [61], particularly for the long-wavelength phonons whose MFP exceeds system size. However, the width dependence for TMD alloys with $L = 5$ μ m breaks from the $W^{1/2}$ trend and displays a $W^{1/3}$ dependence instead, resembling the length dependence in Si-Ge alloy nanowires [40], owing to the interplay between alloy and edge-roughness scattering. Together, these trends stand in contrast to the logarithmic size scaling in graphene [62], which is driven primarily by the ZA branch [35], indicating that heat in TMD alloys is not carried primarily by ZA phonons. For large-width systems, when $L = 5$ μ m the κ_{IP} of MoS_{2-2x}Se_{2x}, WS_{2-2x}Se_{2x}, Mo_{1-x}W_xS₂, and Mo_{1-x}W_xSe₂ is calculated to be 27.3, 27.2, 32.3, and 23.1 W m⁻¹ K⁻¹. We find our $L = 5$ μ m predictions to be slightly larger than similar DFT-BTE predictions [15] of κ_{IP} in $L = 10$ μ m systems Mo_{1-x}W_xS₂. Further, recent calculations [27]

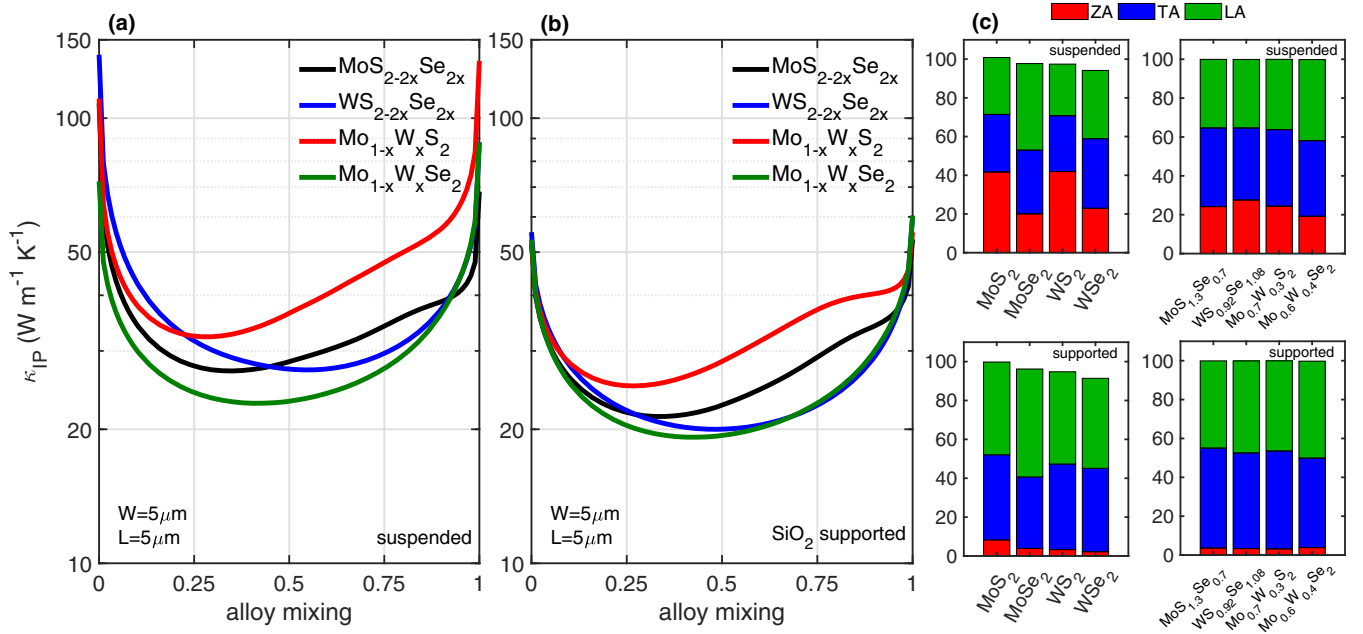


FIG. 3. Room-temperature in-plane thermal conductivity as a function of alloy mixing for suspended (a) and SiO_2 supported (b) $5 \times 5 \mu\text{m}^2$ TMD flakes. The branch-wise phonon percent contributions to thermal conductivity for the homogeneous and alloyed systems is shown in (c). The alloyed compositions in (c) correspond to the mixing amount where the minima occur in (a).

using molecular dynamics (MD) and measurements [23] with time-domain thermoreflectance (TDTR) demonstrate slightly lower values for alloys at similar mixing concentrations for 2D $\text{MoS}_{2-2x}\text{Se}_{2x}$.

We then look at the cumulative κ_{IP} as a function of the phonon MFP $\Lambda_Q = \tau_Q^C v_Q$ in Fig. 2(e). Alloy mass-difference scattering contains both the vDOS and a term quadratic in frequency, resulting in an $\propto \omega^\alpha$ dependence. The exponent α ranges from 2 for long-wavelength ZA phonons whose vDOS is relatively flat to 4 for medium- and short-wavelength LA/TA phonons; therefore, alloy scattering affects high-frequency, short-wavelength phonons much more, while leaving long-wavelength phonons nearly intact with their MFP still limited by anharmonic processes. The resulting effect is that the size scaling of the alloys is overall more gradual, reaching 50% of the maximum κ_{IP} at $\sim 2\text{--}4 \mu\text{m}$, which is far in excess of their MFP whereas the homogeneous TMDs reach 50% of their maximum around $1 \mu\text{m}$ and $100\text{--}200 \text{ nm}$ for the selenide- and sulfide-based TMDs, respectively. Furthermore, remarkably the 50% alloys exhibit non-negligible contributions from long-wavelength phonons where 20% of the total κ_{IP} still comes from phonons with $\Lambda > 20 \mu\text{m}$. The redistribution of contributing MFPs to κ_{IP} in TMD alloys ensures that lower κ_{IP} values can be achieved in larger system sizes which can then be routinely lowered through nanostructuring. We revisit the effects of nanostructuring on supported alloys in a subsequent section.

B. Effects of alloy composition

Next, we calculated the dependence of κ_{IP} on alloy composition in suspended and SiO_2 -supported $5 \times 5 \mu\text{m}$ TMDs in Figs. 3(a) and 3(b). In both suspended and supported TMDs we see a familiar steep decline in κ_{IP} at modest alloying

concentrations reaching broad plateaus with minima in the range of 25% to 75% alloy mixing. From alloy mixing alone in Fig. 3(a), we see a three- to fivefold reduction from the bulk values [Fig. 2(b)] to the alloyed minima at 27, 27.2, 32.3, and 22.88 $\text{W m}^{-1} \text{K}^{-1}$ for $\text{MoS}_{1.3}\text{Se}_{0.7}$, $\text{WS}_{0.92}\text{Se}_{1.08}$, $\text{Mo}_{0.7}\text{W}_{0.3}\text{S}_2$, and $\text{Mo}_{0.6}\text{W}_{0.4}\text{Se}_2$, respectively. When the 2D layers are supported by a SiO_2 substrate, phonons, primarily on the ZA branch [59], are dampened by substrate interactions. As a result, the overall scattering of acoustic modes increases leading to a decrease in the in-plane thermal conductivity. For the homogeneous TMDs we see a two- to threefold reduction in κ_{IP} across all TMDs.

These results for SiO_2 -supported single-layer TMDs agree well with measured values of κ_{IP} TMDs supported on a gold-coated SiO_2 substrate handle [12]. When the supported TMDs are alloyed [Fig. 3(b)] we see a similar dependence as the suspended TMDs, where moderate alloying compositions result in a significant (factor of ~ 2) reduction in κ_{IP} and minima occur between 19.5–25 $\text{W m}^{-1} \text{K}^{-1}$. Predicted values for large-system SiO_2 -supported TMD alloys display very low κ_{IP} , achieving values comparable to suspended TMD nanoribbons in the few-15 nm width range, even at micron sized systems. These significantly low κ_{IP} values for supported TMD alloys are promising for improved thermoelectric performance.

The phonon branch-wise percent contributions for suspended homogeneous (left) and alloyed (right) TMDs are shown in the top two panels of Fig. 3(c). Out-of-plane ZA phonons carry 40% of the thermal conductivity in the sulfides but only about 20% in the selenides where the LA and TA branches contribute roughly 40% each. Upon alloying, which strongly scatters acoustic phonons, the percent contributions are 20% ZA and 80% TA/LA (split roughly evenly) much like the partition seen in the homogeneous selenides. It is

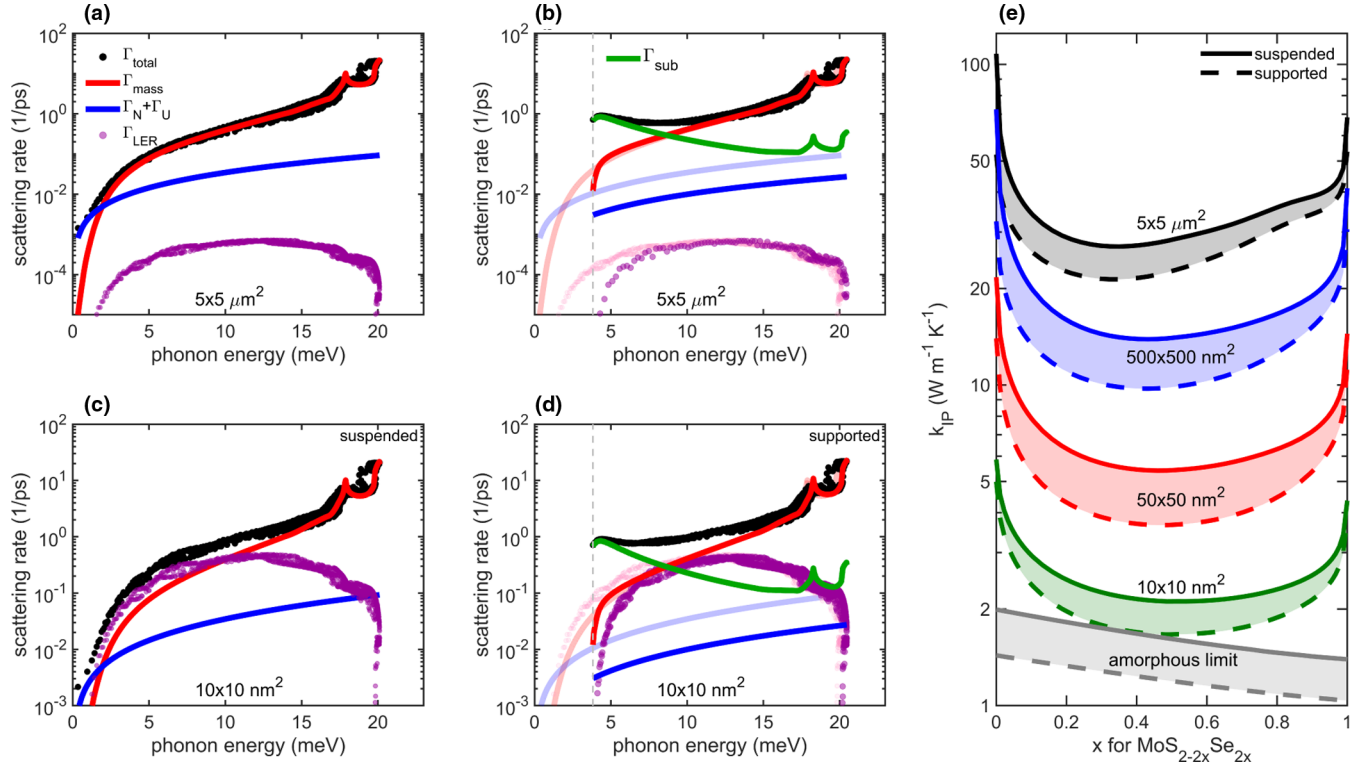


FIG. 4. Here we show the ZA branch total (black dots), mass-difference (red line), anharmonic (blue line), boundary (purple dots), and substrate (green line) scattering rates in large-system ($5 \times 5 \mu\text{m}^2$) and nanoclustered ($10 \times 10 \text{ nm}^2$) suspended and SiO_2 -supported TMD alloys in (a)–(d). Note that we assume suspended systems have no substrate interactions. The room-temperature suspended (solid lines) and supported (dashed lines) in-plane thermal conductivity as a function of alloy composition for $\text{MoS}_{2-2x}\text{Se}_{2x}$ for decreasing system $L \times W$ dimensions is shown in (e).

also worth mentioning here that the AC correction term $\frac{\lambda_1 \lambda_2}{\lambda_3}$ [see Eq. (5)] has a negligible contribution in the alloyed systems, suggesting that an RTA model that accounts for mass-difference scattering rate is sufficient for computing the thermal conductivity in TMD alloys. Branch-wise contributions for SiO_2 supported homogeneous and alloyed systems are shown in the bottom two panels of Fig. 3(c). There we see that the ZA branch contribution in either the homogeneous or the alloyed systems is significantly reduced due to substrate scattering to 10% in MoS_2 and $\sim 5\%$ or less in all other cases. As a result, TA and LA phonons carry roughly 90–95% of the thermal conductivity in substrate-supported systems.

The in-plane thermal conductivity of SiO_2 -supported TMD alloys also exhibits a deviation from the commonly used Matthiessen's rule [63,64]. Matthiessen's rule is an approximation that estimates the total conductivity of a system with multiple scattering sources from the conductivities obtained with the individual scattering sources alone. It is often used when combining contributions from three-phonon scattering, which is dominant in bulk at high temperatures (above 200 K), with impurity or boundary scattering, which dominate in nanostructures and at low temperatures. In our case, we compare the conductivities of suspended alloys [the $x = 0.5$ mixing mark of Fig. 3(a)] and supported nonalloys [the endpoints $x = 0, 1$ mark of Fig. 3(b)] with supported alloys [the $x = 0.5$ mixing mark of Fig. 3(b)]. To that end we can write Matthiessen's rule as

$$\kappa_{\text{alloy, supp}}^{-1} \approx \kappa_{\text{alloy}}^{-1} + \kappa_{\text{supp}}^{-1}, \quad (15)$$

where $\kappa_{\text{alloy, supp}}$, κ_{alloy} , and κ_{supp} represent the thermal conductivity of the supported alloy, suspended alloy, and supported nonalloy, respectively. For a concrete example, we take values from Figs. 3(a) and 3(b); following the $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ curve, we have $23 \text{ W m}^{-1} \text{ K}^{-1}$ for the suspended alloy at the minimum (40% alloy mixing) and $52 \text{ W m}^{-1} \text{ K}^{-1}$ for the substrate supported nonalloy. Following Eq. (15) above, one obtains a value of $16 \text{ W m}^{-1} \text{ K}^{-1}$ for the substrate supported alloy. However, as we can see in Fig. 3 our model predicts the thermal conductivity is roughly $19 \text{ W m}^{-1} \text{ K}^{-1}$ at 40% alloy mixing. Similar deviations are obtained for the other alloys. The breakdown is more stark if we examine the ZA contribution alone: It is 4.3 and $4.4 \text{ W m}^{-1} \text{ K}^{-1}$ in supported MoS_2 and 40% $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ alloy so Matthiessen's rule predicts the ZA contribution in supported alloy to be $2.2 \text{ W m}^{-1} \text{ K}^{-1}$ while our calculation produces only $0.74 \text{ W m}^{-1} \text{ K}^{-1}$.

The reasons we see this breakdown of Matthiessen's rule are twofold: (i) the scattering rates caused by alloy mass-difference and substrate interactions have contrary frequency trends and hence are strongest at opposite ends of the phonon spectrum, and (ii) substrate scattering strongly affects ZA phonons but not in-plane modes while alloy scattering affects all branches. In Figs. 4(a)–4(d) we plot the scattering rates of alloy mass-difference, substrate, line-edge roughness (LER), and anharmonic scattering events for suspended and supported micron- and nanosized systems. Alloy scattering (red line) has an ω^2 dependence in ZA phonons; in contrast, scattering caused by substrate interactions (green line in Figs. 4(c) and 4(d) goes as $1/\omega^2$ [Eq. (A7)] and hence

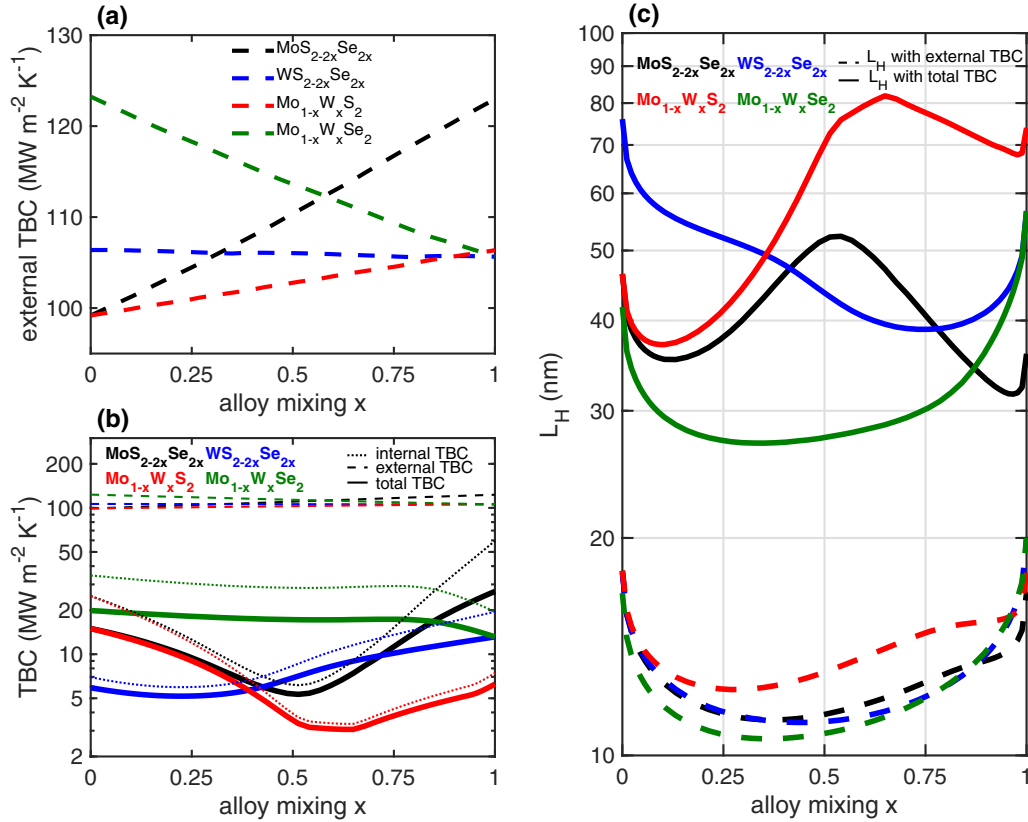


FIG. 5. Room-temperature thermal boundary conductance calculations of TMD alloys on amorphous SiO_2 as a function of alloy composition is shown in (a),(b). The spring coupling constant is $K_a = 4.27 \text{ N/m}$. The thermal healing length as a function of alloy composition is shown in (c).

is strongest at low phonon energies. As a result, the two mechanisms scatter ZA phonons at low and high energies, or large and small wavelengths, leading to a compound effect that is not effectively captured by applying Matthiessen's rule to the respective conductivities.

While alloy mass-difference and substrate scattering scatter short-wavelength (ZA,TA,LA) and long-wavelength (ZA) phonons, respectively, LER scattering is constant across a significant portion of the energy spectrum as seen in Figs. 4(a)–4(e). We explore theoretical minimum thermal conductivities of $\text{MoS}_{2-2x}\text{Se}_{2x}$ in Fig. 4(e) where we show κ_{IP} as a function of alloy mixing at decreasing $L \times W$ dimensions. We see a steady decrease in κ_{IP} as size dimensions are scaled down reaching 4–6 $\text{W m}^{-1} \text{K}^{-1}$ in $50 \times 50 \text{ nm}$ systems. At $500 \times 500 \text{ nm}$ systems κ_{IP} for supported $\text{MoS}_{2-2x}\text{Se}_{2x}$ falls below 15 $\text{W m}^{-1} \text{K}^{-1}$ from ~20–80% Se mixing. Further, for small $10 \times 10 \text{ nm}$ clusters, we find that κ_{IP} nearly reaches the amorphous limit which represents the thermal conductivity of a system with maximum scattering [42,65,66]. For $10 \times 10 \text{ nm}$ sized systems, we take the κ_{IP} to be representative of a supported nanocluster with weak coupling to the substrate such that substrate scattering is negligible.

C. Mass-disorder effects on TBC and healing length

We then calculated the room-temperature through-plane TBC as a function of alloy mixing between TMD alloys and an SiO_2 substrate. For comparison, we assume the vdW

coupling constant between the 2D TMD and SiO_2 substrate is equivalent across all alloy compositions. Density-functional theory calculations estimate the vdW coupling between MoS_2 and quartz- SiO_2 to be 4.27 N/m [67], which we use throughout our calculations. In Fig. 5(a) we show the external TBC which is obtained by assuming the internal scattering (τ_{int}^{-1}) of ZA phonons is very large such that $\tau_{\text{sub}} \gg \tau_{\text{int}}$ and subsequently $\tau_{\text{eff}} \rightarrow \tau_{\text{sub}}$ in Eq. (13). We observe a linear relationship between the external TBC and alloy composition that is representative of the near linear modulation in the atomic mass m_{alloy} and phonon frequencies, which impact the resonant frequency gap ω_0 , substrate scattering rate, and 2D vDOS. However, experimentally measured TBC values do not capture the external TBC due to the presence of additional mechanisms such as internal resistance. Hence, these values overestimate measured TBC. We show the total TBC (solid lines), that accounts for internal resistance, as a function of alloy mixing in Fig. 5(b) where we see values in the range 3–26 $\text{MW m}^{-2} \text{K}^{-1}$ which are in good agreement with reported measurements of uncoated single-layer MoS_2 on SiO_2 [54,68,69]. Our results show a TBC of 6, 13.45, 14.9, and 26.1 $\text{MW m}^{-2} \text{K}^{-1}$ for WS_2 , WSe_2 , MoSe_2 , and MoS_2 on amorphous SiO_2 , respectively.

Upon alloying, the total TBC shows a nonlinear relationship with alloy composition, which is primarily driven by the dependence of the internal resistance (R_{int}) of ZA phonons. The general trend in the internal resistance is represented in the internal TBC ($G_{\text{int}} = R_{\text{int}}^{-1}$) seen as the dotted lines in

Fig. 5(b). We find that the internal TBC (which is governed by τ_{int}) largely follows the alloy composition dependence of the Grüneisen parameter γ [see Eqs. (A1) and (A2)]. As a result, we see a qualitatively different trend and weaker modulation in the TBC as compared to in-plane transport. It is important here to note the significant role of internal resistance on the TBC where we see an order-of-magnitude reduction from the external TBC. The internal resistance may be a concerning thermal bottleneck for cross-plane transport in single-layer 2D devices without encapsulation. However, it has been previously shown that encapsulation and adding multiple 2D layers (which act as encapsulation) can significantly reduce the impact of internal resistance on the TBC [53,55,70]. In either case, our results highlight that alloying can be an effective way of significantly reducing in-plane transport while having minimal impact on cross-plane transport into the substrate.

Lastly, using our values of substrate-supported thermal conductivity and TBC we compute the healing length,

$$L_H = \left(\frac{\kappa t}{G} \right)^{1/2}, \quad (16)$$

as a function of alloying mixing. In a transistor, the healing length represents the distance from source/drain contacts where significant thermal energy can be removed from the active region via the metal source/drain contacts [71]. A longer healing length means there is more lateral heat flow through the source/drain contacts and longer devices can be employed before thermal dissipation is largely cross plane. We plot the healing length taking either the total TBC (solid lines) or external TBC (dashed lines) into consideration as a function of alloy mixing in Fig. 5(c). The healing length determined by the external TBC alone follows well the dependence of κ_{IP} reaching a minimum around 12–16 nm for most of the alloy composition range. However, including the internal resistance we see that the healing length increases noticeably and exhibits a different trend for some alloys. We report healing lengths between 35–75 nm for the homogeneous TMDs and minima of 27 nm and 39 nm for $\text{Mo}_{0.54}\text{W}_{0.46}\text{Se}_2$ and $\text{WS}_{0.52}\text{Se}_{1.48}$. As for $\text{MoS}_{2-2x}\text{Se}_{2x}$ and $\text{Mo}_{1-x}\text{W}_x\text{S}_2$, the healing length decreases steeply for small amounts of alloy mixing but then begins increasing slowly around 12–14% reaching maxima near 54% and 65%, respectively. This suggests that for devices that employ alloyed TMDs, device lengths must be roughly 90–240 nm ($\sim 3L_H$) or smaller in order to see significant heat sinking through the source/drain contacts [71].

IV. CONCLUSION

We have calculated the in-plane thermal conductivity of suspended and substrate supported transition metal dichalcogenide alloys (MX_2 : $\text{M} = \text{Mo}, \text{S}$ and $\text{X} = \text{S}, \text{Se}$). Our results show that alloy scattering substantially reduces both suspended and supported in-plane thermal conductivity of TMD alloys, even at modest alloy compositions. The lowest values are typically two to three times lower than the nonalloyed constituents. Surprisingly, despite dominant alloy scattering, the thermal conductivity of suspended alloys is dependent on system size up to several microns, far exceeding the phonon MFP, but the dependence is much more gradual than in

nonalloyed systems, owing to contributions from long-wavelength phonons. ZA phonon contributions to thermal conductivity are significantly reduced by substrate scattering. As a result, TA/LA phonons carry 90–95% of the thermal conductivity in supported TMDs. We see a breakdown of Matthiessen's rule for supported TMD alloys whose thermal conductivities cannot be estimated by combining the conductivities of supported homogeneous TMDs and the suspended TMD alloys. We also calculate the thermal boundary conductance between the alloyed 2D layer and a SiO_2 substrate. Our results show that the alloy dependence of the thermal boundary conductance is qualitatively different than for in-plane thermal conductivity. We conclude here that alloying combined with nanostructuring is a powerful way to tune the thermal properties of TMDs and a promising avenue toward achieving low thermal conductivity. Conversely, device applications requiring good heat removal will benefit from improved TBC to the substrate.

On the outlook of TMD alloys as thermoelectric materials, we note that the reduction of thermal conductivity in large (100s nm to micron sized) systems may not be sufficient to obtain a high ZT for monolayer TEs. However, we can reduce thermal conductivity further, achieving a better ZT, by employing superlattice and nanodomain structures with sub-50-nm size features, which have been experimentally realized [72,73]. Further, the effects of alloy scattering of electrons may present an additional challenge for TMD alloy based thermoelectrics. Alloy scattering of electrons is proportional to the alloy scattering potential ΔU_{alloy} , which is related to the difference between electron affinities of the constituent homogeneous materials [74]. If $\Delta U_{\text{alloy}} < 150$ meV then alloy scattering has negligible impact on the phonon-limited mobility of TMDs [74]. Although the electron affinity can be readily obtained from first principles [75], effects of the fabrication process and substrate features may impact the electron affinity of fabricated devices [76]. Thus, we note that careful attention to alloy scattering of electrons in TMD alloy systems may be required to maximize the benefits of alloying in TEs. Lastly, strong charge impurity scattering of electrons is a concern for substrate supported monolayers [77] and could therefore hinder their TE performance. Hence, few-layer structures are preferred for improved electron mobility for substrate supported 2D systems [34].

We note that thickness-dependent thermal conductivity of homogeneous vdW materials has been studied [78] where nonmonotonic [79,80] (decreasing then increasing) and monotonically increasing [81,82] trends have been shown for suspended and substrate-supported systems with increasing thickness. The thickness dependence of alloyed vdWs systems has not been studied. We expect that the reduction in in-plane conductivity by alloy scattering could lead to a substantially weaker thickness dependence of thermal conductivity for TMD alloys. However, the full calculation thermal transport in few-layered alloys is beyond the scope of the present work and may be the subject of future investigation. Based on the above, we suggest that mono- and few-layered TMD alloy superlattices or TMDs with alloyed nanodomains that minimize thermal conductivity while retaining phonon-limited electron mobility may be a promising avenue for improved 2D TMD thermoelectrics.

ACKNOWLEDGMENT

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APPENDIX

1. First-principles phonon dispersion calculations

We calculate the full phonon dispersion of four homogeneous transition metal dichalcogenide monolayers (MoS₂, MoSe₂, WS₂, and WSe₂) using density-functional perturbation theory (DFPT) as implemented within the PHonon code as distributed with the open-source package QUANTUM ESPRESSO [37,38]. The details for the phonon dispersion calculation of MoS₂ can be found in our previous work [36]. Phonon calculations of single-layer, 1H-phase homogeneous MoSe₂, WS₂, and WSe₂ are performed through DFPT [38]. For MoSe₂ we used a nonrelativistic Martins-Troullier pseudopotential with a Perdew-Burke-Ernzerhof/generalized gradient approximation (PBE/GGA) [83] functional. We relax the unit cell structure on an offset $6 \times 6 \times 4$ Monkhorst-Pack grid with a plane wave energy cutoff of 140 Ry and a self-consistent field convergence threshold of 10^{-14} Ry. In calculating the phonon dispersion of WS₂ and WSe₂ we used a scalar relativistic Vanderbilt ultrasoft pseudopotential with a PBE/GGA functional. The structures are relaxed on an offset $27 \times 27 \times 1$ and $16 \times 16 \times 1$ MP grids for WS₂ and WSe₂, respectively, with a plane wave energy cutoff of 100 Ry and a self-consistent field convergence threshold of 10^{-14} Ry. All structures are relaxed until the forces on atoms are all less than 5×10^{-4} eV/Å. After structural optimization, we calculate the dynamical matrices using a $6 \times 6 \times 4$ Monkhorst-Pack grid for MoSe₂ and a $8 \times 8 \times 1$ MP grid for both WS₂ and WSe₂. We then inverse Fourier transform the dynamical matrices into real space onto a dense grid of 126 040 q points, which contains the set of 25 208 equidistant q points plus grid points for a 2D central difference method around each equidistant point ($4 \times 25\,208 + 25\,208 = 126\,040$).

2. Three-phonon scattering rates

In bulk homogeneous materials, phonon transport is governed by anharmonic normal and Umklapp scattering. The three-phonon normal and Umklapp scattering rates used here follow the work of Morelli *et al.* [84] and have been adapted to 2D materials [35] where good agreement with measured thermal conductivity of graphene was found. In this formalism, $1/\tau_Q^N = B_N \omega_Q^{a_N} T^{b_N} e^{-\Theta_j/3T}$ and $1/\tau_Q^U = B_U \omega_Q^{a_U} T^{b_U} e^{-\Theta_j/3T}$, where the prefactor terms B_N and B_U are written as

$$B_N(a_N, b_N) = \left(\frac{k_B}{\hbar}\right)^{b_N} \frac{\hbar \gamma_j^2 [S_0 h_{2D}]^{(a_N+b_N-2)/3}}{\bar{M} v_j^{a_N+b_N}}, \quad (\text{A1})$$

and

$$B_U(a_U, b_U) = \frac{\hbar \gamma_j^2}{\bar{M} v_j^{a_U} \Theta_j^{b_U}}, \quad (\text{A2})$$

respectively. In the above equations, Θ_j is the branch-wise Debye temperature, γ_j is the branch-wise Grüneisen parameter, S_0 is the surface area of the 2D layer unit cell ($S_0 = \frac{\sqrt{3}}{2} a_0$

for homogeneous TMDs or $S_0 = \frac{\sqrt{3}}{2} a_{\text{alloy}}$ for alloyed TMDs), and $\bar{M}$ is the unit cell atomic mass. The empirical exponential factors a_N , b_N , a_U , and b_U that determine the frequency and temperature dependencies for normal and Umklapp scattering are $a_N = [1\ 2\ 2]_j$, $b_N = 1$, $a_U = 2$, and $b_U = 1$, respectively.

Normal and Umklapp scattering typically dominate in bulk crystals where system dimensions are large and impurities/defects are low in concentration, however here we are interested in studying phonons in the presence of boundaries of alloyed materials. Hence, strong boundary scattering from nanostructuring and mass-difference scattering from alloying will dominate over three-phonon (N and U) processes and determine the effective relaxation time of phonons. The remaining scattering mechanisms can be grouped as mass-disorder scattering (τ_{iso}^{-1} , τ_{imp}^{-1} , and τ_{mass}^{-1}) and extrinsic boundary/interface scattering (τ_{LER}^{-1} and τ_{sub}^{-1}).

The mode-dependent Grüneisen parameters, which determine the anharmonicity of phonon-phonon interactions [7], are obtained using

$$\gamma(Q) = -\frac{a_0}{2\omega_0} \frac{\partial \omega_Q}{\partial a}, \quad (\text{A3})$$

where a_0 and ω_0 are the equilibrium lattice constant and phonon frequencies, respectively. We then average the mode-dependent Grüneisen parameters over the heat capacity to obtain a temperature-dependent Grüneisen parameter per branch [85],

$$\gamma_j(T) = \frac{\sum_Q \gamma(Q) C_v(\omega_Q, T)}{\sum_Q C_v(\omega_Q, T)}. \quad (\text{A4})$$

We use this branch-wise $\gamma_j(T)$ when calculating the normal and Umklapp scattering rates [see Eqs. (A1) and (A2)]. When we alloy mix two TMDs, we apply the VCA on the strained phonon dispersions and then use them to recalculate the Grüneisen parameter for the alloyed material.

3. Extrinsic edge roughness and substrate scattering mechanisms

Our model also includes phonon scattering due to rough line-edge boundaries $1/\tau_Q^{\text{LER}}$ at the 2D layer's planar edge and, when supported by a substrate, interactions between flexural ZA phonons and the underlying substrate $1/\tau_Q^{\text{sub}}$. In considering scattering due to line-edge roughness, phonons collide with the boundary provided they have not already scattered internally where each collision with the boundary is treated with a momentum-dependent specularity parameter $p(\mathbf{q}) = \exp(-4q^2 \Delta \sin^2 \theta_B)$. The specularity parameter determines how specular or diffuse the collision event is based on the root-mean-square (rms) roughness Δ , wave vector $q^2 = |\mathbf{q}|^2$, and angle of incidence θ_B . We use an rms edge roughness $\Delta = 0.45$ nm for all calculations. Line-edge roughness (LER) scattering [35,86] can be written as

$$\frac{1}{\tau_Q^{\text{LER}}} = \frac{v_Q^\perp}{W} \frac{F_Q}{[1 - (\Lambda_Q^{\text{int},\perp}/W) F_Q]}, \quad (\text{A5})$$

where W is the width of the nanoribbon, $v_Q^\perp$ are the phonon group velocities perpendicular to the flow of transport (i.e., toward the boundary), and $\Lambda_Q^{\text{int},\perp} = v_Q^\perp / \tau_Q^{\text{int}}$ is the phonon MFP

perpendicular to the direction of transport. Here, $1/\tau_Q^{\text{int}}$ represents the scattering rate of all internal mechanisms, including three-phonon $N + U$ processes, mass-disorder, isotope, impurity, and substrate scattering when supported by a substrate. The form factor F_Q is written as

$$F_Q = \frac{[1 - p(\mathbf{q})][1 - \exp[-W/\Lambda_Q^{\text{int},\perp}]]}{1 - p(\mathbf{q})\exp[-W/\Lambda_Q^{\text{int},\perp}]} \quad (\text{A6})$$

This model captures the interplay between internal scattering mechanisms and boundary roughness scattering and has been previously used to model line-edge roughness in graphene nanoribbons [86]. Beyond phonon collisions with line-edge boundaries, in-plane phonons traveling in a substrate supported 2D layer also interact with the surface roughness of the substrate leading to an additional scattering mechanism

[59]. We can write the substrate scattering rate in the following manner,

$$\frac{1}{\tau_{\text{sub}}(\omega)} = \frac{\pi}{2} \left(\frac{D_{\text{sub}}(\omega)}{m_{\text{sub}}m_{\text{alloy}}} + \frac{D_{2\text{D}}(\omega)}{m_{\text{alloy}}^2} \right) \frac{K_a^2}{\omega^2} \quad (\text{A7})$$

In the above, $D_{\text{sub}}(\omega)$ is the phonon density of states of the supporting substrate (SiO_2 here), m_{sub} is the mass of atoms on the surface of the substrate, and K_a is the van der Waals (vdW) spring coupling constant. This form of the substrate scattering rate ensures that the net heat flux across the 2D-3D interface is zero and hence, any phonon that hops from the 2D layer to the substrate must hop back or be replaced by an equivalent phonon from the substrate.

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