Structure-Property Relationships

Effects of Defects on the Temperature-Dependent Thermal Conductivity of Suspended Monolayer Molybdenum Disulfide Grown by Chemical Vapor Deposition

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It is understood that defects of the atomic arrangement of the lattice in 2D molybdenum disulfide (MoS₂) grown by chemical vapor deposition (CVD) can have a profound effect on the electronic and optical properties. Beyond these it is a major prerequisite to also understand the fundamental effect of such defects on phonon transport, to guarantee the successful integration of MoS₂ into the solid-state devices. A comprehensive joint experiment-theory investigation to explore the effect of lattice defects on the thermal transport of the suspended MoS₂ monolayer grown by CVD is presented. The measured room temperature thermal conductivity values are 30 \pm 3.3 and 35.5 \pm 3 W m⁻¹ K⁻¹ for two samples, which are more than two times smaller than that of their exfoliated counterpart. High-resolution transmission electron microscopy shows that these CVD-grown samples are polycrystalline in nature with low angle grain boundaries, which is primarily responsible for their reduced thermal conductivity. Higher degree of polycrystallinity and aging effects also result in smoother temperature dependency of thermal conductivity (κ) at temperatures below 100 K. First-principles lattice dynamics simulations are carried out to understand the role of defects such as isotopes, vacancies, and grain boundaries on the phonon scattering rates of our CVD-grown samples.

transition-metal dichalcogenide (TMD) semiconductors as a graphene alternative. Molybdenum disulfide (MoS₂), as a promising member of the TMDs family, exhibits thickness-dependent indirect-todirect bandgap crossover due to quantum confinement,^[1] leading to a distinct photoluminescence^[1-3] and a high on-off ratio of a field effect transistor.^[4] Other intriguing properties that highlight monolayer MoS₂ as an excellent candidate to integrate into next-generation nanoelectronics, optoelectronics, and spintronic devices include high electron mobility^[5] and significant spin-orbit coupling as a consequence of strong valley polarization.^[6] Moreover, large and tunable Seebeck coefficient of MoS2 monolayer makes it possible to implement this material in thermoelectric applications.^[7–9] To achieve mass production of these functional devices, wafer-scale and high-quality synthesis of MoS₂ monolayer films is vital. It has been well documented that chemical vapor

1. Introduction

The lack of an intrinsic electronic bandgap in graphene, which strongly impedes its application in modern solid-state devices, has stimulated enormous interest in atomically thin

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well documented that chemical vapor deposition (CVD) is an effective route to synthesize large scale MoS₂ films.^[10] However, due to growth process imperfections, CVD-grown MoS₂ monolayer exhibits notable heterogeneity including vacancies, dislocation cores, substitutional dopants, misoriented grains, etc., compared to its single-crystalline

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exfoliated counterpart.^[11–13] These unintentional defects perturb the lattice arrangement in the MoS₂ monolayer, leading to defect-induced localized states that profoundly alter its electronic and optical transport characteristics.^[14–18] Electron transport measurements have demonstrated that vacancies^[19,20] and grain boundaries^[21] have remarkable effects on the charge mobility of the as-synthesized MoS₂ monolayer. For example, mobility values of ≈45 cm² V⁻¹ s⁻¹ were reported for MoS₂ grown by CVD^[22] on silicon dioxide, which is about two times smaller compared to the value of ≈81 cm² V⁻¹ s⁻¹ reported for mechanically exfoliated^[19] MoS₂ at room temperature. On the other hand, the thermal conductivity (κ) of CVD-grown MoS₂ monolayers remains unknown, which is crucial for the successful development of MoS₂-based technological applications.

Compared to extensive research efforts on the electrical and optical properties, experimental demonstration on temperature dependency of thermal conductivity of MoS₂ monolayer in general and particularly CVD-grown film, which is more desired for industrial applications, is notably lacking due mostly to technical challenges in sample preparation and measurements. To this date, the thermal conductivity of the MoS₂ monolayer has been measured using Raman thermometry only at room temperature for exfoliated flake to be 34.5 ± 4 ,^[23] 62.2,^[24] and $84 \pm 17^{[25]}$ W m⁻¹ K⁻¹ and for CVD-grown flake in the very recent investigation to be $13.3 \pm 1.4^{[26]}$ W m⁻¹ K⁻¹. The noticeable discrepancy in the reported values has mainly been attributed to the differences in the laser power dependent optical absorption coefficient of the MoS₂ flake and phonon coupling between the flake and corresponding substrate. Moreover, none of these works has provided a detailed correlation between the measured thermal conductivity and the structure of their monolayer flake. Such correlation is paramount for understanding transport physics in such 2D systems as it is evident by the many papers reporting on their electrical and optical properties where intrinsic structural defects and their effects on transport mechanism cannot be ignored.^[11,12] On the other hand, in the recent years an increasing number of atomistic calculations have been done to theoretically predict the thermal conductivity of the MoS₂ monolayer and a wide range of thermal conductivity at room temperature, that is, $\kappa = 23.2-155$ W m⁻¹ K⁻¹ has been reported.^[8,27-31] Moreover, it was demonstrated theoretically that defects such as vacancies and isotopes suppress the thermal conductivity of monolayer MoS₂. For example, molecular dynamic (MD) simulations^[32] showed that introducing vacancies to the lattice structure of MoS₂ keeps phonon specific heat and group velocity almost unchanged but decreases phonon relaxation time compared to its pristine form. Calculation based on firstprinciples^[29] revealed that phonon group velocities are significantly lower near the vacancy-induced quasi-localized phonon modes. Also, isotopes were found to strongly scatter phonons with intermediate frequencies in the large-size MoS₂ samples where boundary scattering has a minor effect.^[33] All these illustrate the necessity in obtaining reliable experimental demonstration of thermal conductivity in a wide temperature range accompanied with well-matched atomistic calculations and solid structural characterization to discover the phonon transportstructure link in CVD-grown MoS2 monolayers and shed light on the scope of implementation of this promising atomically thin semiconductor as a potential graphene alternative.

Here, we have utilized a microdevice with integrated resistance thermometers to report the first experimental data on the thermal conductivity of suspended CVD-grown MoS₂ monolayers in a wide temperature range. Transmission electron microscopy (TEM) was used to characterize the material structure of the measured samples to understand how defects in the lattice atomic arrangement affect thermal transport. To explain quantitatively the effects of the atomic scale defects on the phonon scattering rates, first-principles lattice dynamics calculations were performed to evaluate the role of isotopes, vacancies, and grain boundaries. For two separately prepared samples, the thermal conductivity of 30 ± 3.3 and $35.5 \pm 3 \text{ W m}^{-1} \text{ K}^{-1}$ are obtained at room temperature. The TEM images reveal that these samples are polycrystalline in nature with low angle grain boundaries. The sample with higher degree of polycrystallinity exhibits smoother temperature dependency at lower temperature that indicates the significant role of grain boundaries at these temperatures. The results obtained in this work deepen our fundamental understanding of the underlying thermal transport mechanism in CVD-grown MoS₂ monolayer and facilitate its successful integration into high-performance solid-state devices, where thermal management is imperative.

2. Results and Discussion

We grew monolayer MoS₂ sheets on Si/SiO₂ substrates by the CVD technique (see the Experimental Section). Briefly, a SiO₂/ Si wafer is placed upside-down above a powdered transition metal precursor (MoO₃) inside a quartz tube under nitrogen flow. The chalcogen (S) is placed upstream in a cooler region of the tube. When the temperature is raised to ≈ 700 °C in the central portion of the furnace, both the MoO3 and S are cosublimated and MoS2 growth begins on the substrate. The as-grown MoS₂ islands are generally observed to be triangular in shape (Figure 1a). Characterization by scanning tunneling electron microscopy (STEM) confirmed the trigonal prismatic structure of MoS₂ and that the as-deposited films are monolayer (Figure 1b) with a thickness of about 0.66 nm measured by atomic force microscopy (AFM) as shown in Figure 1c. The suspended microdevice platform^[34,35] that was developed for probing thermal and thermoelectric properties of nanostructures is utilized here to measure the intrinsic thermal conductivity of suspended MoS2 monolayers in a wide range of temperature. The heart of this device is two adjacent lowstress silicon nitride (SiN_x) membranes, each of which is suspended by six long SiN_x beams over a through-substrate hole. Figure 1d,e illustrates two samples, denoted as sample 1 and sample 2, respectively, that were successfully assembled on the membranes.

The through-substrate hole under the membranes allowed us to conduct high-resolution transmission electron microscopy (HRTEM) characterization on the same sample from which the thermal properties were measured. Therefore, following the thermal measurements, the sample was removed from the cryostat, and its crystal structure was characterized by HRTEM. To evaluate the degree of crystallinity, selected area electron beam diffraction (SAED) patterns were taken in three different regions on the suspended segment of each SCIENCE NEWS ______ www.advancedsciencenews.com





Figure 1. Structural characteristics of the samples. a) Scanning electron microscopy (SEM) image of as-deposited MoS₂ sheets on SiO₂/Si substrate. b) Typical scanning transmission electron microscopy (STEM) image of the as-deposited sheets. c) An AFM image of the MoS₂ monolayer showing a thickness of ≈ 0.66 nm. SEM images of d) sample 1 and e) sample 2. Selected area electron diffraction patterns of different regions on suspended segment of f-h) sample 1 and i-k) sample 2. The grain angles of $\Delta \theta_{1-2} = 18 \pm 1^{\circ}$ for sample 1 in (g), $\Delta \theta_{1-2} = 7 \pm 1^{\circ}$ and $\Delta \theta_{1-3} = 33 \pm 1^{\circ}$ for sample 2 in (j) are observed between different numbered patterns. High-resolution TEM images of MoS₂ monolayer in l) sample 1 and m) sample 2. The presence of amorphous layer is clearly observed on the samples. The lines show the (100) planes with lattice fringes spacing of 0.26 nm. The circled fringe shows different grain orientation. n) Raman spectra of a transferred and supported MoS₂ flake (dashed line) and the suspended segment of sample 2 (solid line).

sample as shown in Figure 1f-h and Figure 1i-k for samples 1 and 2, respectively. Some regions (Figure 1f,k) consist of one set of hexagonal Bragg reflections in their SAED pattern that indicates these regions are single-crystalline. While, the polycrystalline nature of the other regions (Figure 1g-j) with low angle grain boundaries is illustrated by the existence of more than one set of hexagonal Bragg reflections in their corresponding SAED patterns. It thus can be concluded that even

though our two samples belong to the same growth batch, not only their crystal structure is different but also the degree of crystallinity is not uniform across one sample. In general, sample 1 showed less misorientation than sample 2 that is indication of better crystallinity in sample 1. The HRTEM of Figure 1l,m show the lattice fringes with a spacing of 0.26 nm for samples 1 and 2, respectively. The slight misorientation of the lattice fringes as evident by Figure 1l, also confirms the



existence of several slightly misoriented grains, validating their polycrystalline nature. Furthermore, these images also show the presence of an amorphous-like layer on both samples. We anticipate that this is due to two main reasons. It is well understood that CVD-grown MoS₂ monolayers undergo aging effect due to oxidation^[36] that can form such layer. Also, it can originate from the poly(methyl methacrylate) (PMMA) residues left on the sample surface as reported for graphene,^[37] h-BN,^[38] and multilayer exfoliated $MoS_2^{[39]}$ prepared by the same technique. To further study the structure of the samples, Raman spectroscopy was carried out. Sample 1 was unfortunately broken after TEM characterization and the Raman spectra presented here were taken from the suspended segment of sample 2 as well as another MoS₂ monolayer flake transferred by the same PMMA technique on a platinum (Pt) substrate. The Raman signal intensity of suspended MoS₂ is limited by the laser power since higher laser power was found to damage the suspended sample in this study. For the MoS₂ monolayer flake on the Pt substrate, higher laser power can be used to obtain better Raman signal as the laser-generated heat can be efficiently removed by the Pt substrate. As shown in Figure 1n two prominent peaks around 386 and 411 cm-1 for the supported and 380 and 408 cm⁻¹ for the suspended flakes were observed, which correspond to the in-plane $E_{2\sigma}^1$ and out-ofplane A_{1g} modes, respectively.^[40,41]



To obtain the thermal conductivity of the samples, we need to convert the measured thermal resistance to the intrinsic thermal conductivity. The measured thermal resistance of the sample (R_t) contains contributions from the intrinsic thermal resistance (R_i) , the contact thermal resistance (R_c) , and the internal thermal resistance of the two membranes that originates from nonuniformity in temperature distribution on the membranes (R_{m0}), that is, $R_t = R_i + R_c + R_{m0}$. To calculate R_c we use an expression derived in ref. [38] based on a fin heat transfer model and the values of $R_{\rm m0}$ were obtained from a numerical calculation carried out with a finite element software (COMSOL) (see the Supporting Information). Temperaturedependent total, contact, and internal thermal resistances of both samples are shown in Figure 2a,b. For sample 1 and sample 2, the obtained R_c at room temperature reached 14 and 17% of the measured R_t , respectively. Also, R_{m0} is at least one order of magnitude smaller than R_t in the whole temperature range. These findings are in agreement with previous results on suspended few-layer exfoliated MoS2.[39] Then the obtained $R_{\rm c}$ and $R_{\rm m0}$ were subtracted from the $R_{\rm t}$ to find the $R_{\rm i}$ and consequently the thermal conductivity (κ) values by taking account of the dimensions of the suspended segment of the samples as listed in Table 1.

Figure 2c shows the thermal conductivity as a function of temperature for both samples measured in this work. At



Figure 2. Temperature-dependent total (circles), contact (squares), and internal (triangles) thermal resistances for MoS_2 monolayer in a) sample 1 and b) sample 2. c) Experimental in-plane thermal conductivity of MoS_2 monolayer in sample 1 (circles) and sample 2 (squares) as a function of temperature. $T^{1.38}$ and $T^{1.24}$ trends of κ for sample 1 and 2, respectively, at temperatures less than 100 K are shown by the fitting lines.

 Table 1. Dimensions of the suspended segment of the samples measured in this work.

	Suspended length [µm]	Width [µm]	Thickness [nm]
Sample 1	1.31 ± 0.06	$\textbf{8.38} \pm \textbf{0.89}$	$\textbf{0.66} \pm \textbf{0.1}$
Sample 2	1.1 ± 0.063	10.8 ± 0.63	$\textbf{0.66} \pm \textbf{0.1}$

300 K the obtained thermal conductivity values are 30 \pm 3.3 and 35.5 \pm 3 W m⁻¹ K⁻¹ for samples 1 and 2, respectively. Indeed, these values are comparable to those reported by Yan et al.^[23] and more than two times smaller than the value of $84 \pm 17^{[25]}$ W m⁻¹ K⁻¹ for exfoliated monolayer MoS₂ sample prepared with a PMMA-assisted transfer technique whereas they are still higher than the value of $13.3 \pm 1.4^{[26]}$ W m⁻¹ K⁻¹ for CVD-grown and PMMA-free monolayer MoS₂ sample, all measured with the Raman thermometry. While the notable discrepancy between the κ values reported in refs. [23,25] and [26] has mainly been attributed to the difference in the absorption coefficient of the sample, we believe the crystal quality of the samples play a significant role on the phonon behavior. It is well-understood that the crystal quality, and therefore grain size, of CVD grown 2D TMDs can vary significantly depending on the growth conditions. This effect can be even more significant when comparing CVD-grown samples to their exfoliated equivalents. For example, it is documented that defects in suspended CVD-grown graphene cause the reduction of thermal conductivity when compared to its defect-free single-crystalline counterpart.^[42,43]

Another interesting trend of our results is that at temperatures lower than 100 K, both samples exhibit temperature dependence of the thermal conductivity different from theoretical 3D crystals where $\kappa \propto T^3$. It is known that in 3D crystals, the thermal conductivity should theoretically scale with T^3 at very low temperatures because the anharmonic phonon scattering is very weak at low temperatures and heat capacity scales with temperature as T^3 due to linear acoustic phonon dispersion (Debye model) at low frequencies and 3D density of states.^[44] For 2D materials, however, the existence of the quadratic flexure (out-of-plane) phonon modes and the 2D density of states can lead to a different scaling law of thermal conductivity at low temperatures.^[33,45,46] Our analyses indicate that the quadratic branch itself will lead to a thermal conductivity scaling with temperature as $\approx T^{1.50}$ when considering weak anharmonic scattering and thus fixed phonon mean free paths. The other two linear acoustic phonon branches will lead to thermal conductivity scaling approximately as $T^{2.00}$. Adding all three acoustic branches together, we find a total thermal conductivity scaling with temperature as $\approx T^{1.54}$ (see the Supporting Information). The experimentally observed low-temperature (<100 K) thermal conductivity follows $T^{1.24-1.38}$ (Figure 2c), which is slightly lower than the theoretically predicted $T^{1.54}$.

Effects such as defects may have influenced such scaling relations, especially those that affect the scattering of phonons of varying frequencies, leading to the above-mentioned discrepancy between theory and experiments. It is well understood that when using the PMMA-assisted transfer technique to assemble such atomic thin samples, the PMMA does not dissolve completely, and leaves residue on the surface that can affect thermal transport in 2D materials.^[37] This can result in lower phonon mean free path due to partially diffuse phonon-surface scattering that depends on the specularity parameter (*p*) that varies on the degree of surface contamination.^[39] Besides this, native oxide as a surface disorder is considered as another source of diffuse phonon-surface scattering.^[47,48] Even though MoS₂ has the mechanical strength three times stronger than that of steel,^[49] suspension of its monolayer is quite challenging. We were able to successfully transfer the sample 1 into the microdevice and preform the thermal measurement two weeks after its growth date, while the preparation and measurements of the sample 2 were done about two months after its initial growth. Therefore, it can be expected that the sample 2 has experienced more oxidation on its surface and grain boundaries.^[36] Furthermore, the variation of the crystallinity between the two samples yields a variation in the grain boundary concentration. Just the presence of the grain boundaries was recently found to be responsible for reducing the in-plane thermal conductivity of 5 nm thick polycrystalline MoS₂ film to 0.73 \pm 0.25 W m⁻¹ K⁻¹ in the temperature range of 320-430 K.^[50] Even though grain boundary scattering of phonons has long been considered to be frequency independent by the gray model, Wang et al.^[51] suggested that this is not the case and there is actually a phonon frequency dependence transmission coefficient through grain boundaries, that leads to a frequency-dependent mean free path when phonons are scattered by grain boundaries. Such an observation was also demonstrated for graphene, where the thermal conductance across various defects such as grain boundaries and line defect have different temperature dependencies due to their different phonon transmission spectra.^[52]

To evaluate the effect of vacancies and grain boundaries, we have incorporated these factors into our first-principles calculation (see the Experimental Section). Natural isotope scattering has also been included in all calculations according to Tamura's equation.^[53,54] According to ref. [55], the vacancy scattering is similar to isotope scattering but with an effective mass instead of the actual atomic mass. For grain boundary scattering, we assume that the boundary scattering is diffusive to all phonons, and a length scale was applied to limit the mean free path of all phonons. It is seen from Figure 3 that the grain boundary scattering is necessary to bring the thermal conductivity down to the range of experimental data, and the estimated grain size is on the order of 1-1.5 µm. The TEM analyses indicated an average grain size of \approx 500 nm, which is smaller than the above prediction. This is likely because we have assumed that all phonons are diffusively scattered by grain boundaries and thus the upper limit of mean free path is the grain size. However, since long wavelength phonons are much less affected by the grain boundaries due to large transmission compared to short wavelength phonons, the lumped effect should display an effective grain size larger than the actual grain sizes. The addition of vacancy scattering slightly flattens out the temperature profile (e.g., L = 1500 nm, Figure 3) besides decreasing the thermal conductivity values collectively. However, the calculations are not able to completely capture the slope difference in the temperature dependence at low temperatures between the two samples. This discrepancy may be attributed to the difference in the line defect concentrations between the samples. As explained earlier in the HRTEM analysis, even though both sample exhibit





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Figure 3. Thermal conductivity from first-principles calculations for different boundary scattering length as a function of temperature a) without and b) with %0.01 vacancy concentration of Mo atoms. The results are under influence of natural isotope scattering effects.

low angle grain boundaries, sample 2 exhibits higher degree of grain misorientation compared to sample 1. This is expected to generate higher concentration of line defects, which was theoretically shown to have a greater impact than grain boundaries in suppressing thermal conductivity especially at low temperatures, for both single-layer MoS₂ and graphene.^[52,56]

3. Conclusion

In summary, we used a suspended microdevice with integrated resistance thermometers to probe the intrinsic thermal conductivity of MoS₂ monolayer grown by CVD in the temperature range of 10-475 K. First-principles lattice dynamics calculations were performed to interpret the exprimental results and quantitatively explain the effects of the atomic scale defects such as isotopes, vacancies, and grain boundaries on the phonon scattering rates. More defect concentration in the CVDgrown MoS₂ monolayer compared to its single-crystalline exfoliated counterpart leads to reduction in thermal conductivity at 300 K by more than 50%. The HRTEM characterizations reveal that our samples are polycrystalline in nature with low angle grain boundaries. Higher degree of polycrystallinity results in smoother temperature dependency at low temperature (<100 K) that indicates the paramount role of grain boundaries at these temperatures. Moreover, the theoretical analysis at the long wavelength limit provided useful insight to the thermal conductivity scaling relation with temperature at low temperatures where long wavelength phonons dominate the thermal transport. Overall, our results uncover the fundamental structurethermal conductivity link in CVD-grown MoS2 monolayer highlighting its potential to integrate into modern solid-state devices.

4. Experimental Section

Synthesis of MoS_2 : Monolayer MoS_2 sheets were grown on \approx 300 nm SiO₂/Si wafers in a 2 in. CVD furnace, with \approx 20 mg of MoO_3 and \approx 200 mg of sulfur. The furnace temperature was ramped to \approx 700 °C at a rate of \approx 18 °C min⁻¹, then kept at \approx 700 °C for \approx 10 min, while flowing

ultrahigh purity nitrogen gas at \approx 50 sccm. After the reaction, the furnace lid was opened to naturally cool the furnace to room temperature.

Thermal Measurements: The suspended microdevice shown in Figure 1d, e consists of two adjacent low-stress silicon nitride (SiN_x) membranes, each of which is suspended by six long SiN, beams over a through-substrate hole. A Pt serpentine line was fabricated on each membrane that serves as heater and resistance thermometer (RT). To transfer the MoS₂ monolayer flake on the device so that it bridges the two membranes, a method based on a PMMA carrier layer^[57] as shown in previous works was used.^[58] The MoS₂ flakes selected for transfer from the growth substrate were of single layer and triangular form. After the PMMA transfer process, the viscous forces exerted on the assembled sample by the acetone during the drying process caused the sample to deform or tear at the edges. The structural characterizations validate the dimensions and integrity of the sample. The thermal measurement was conducted in a high-vacuum cryostat so that air conduction and convection between the two membranes is eliminated. Before conducting the thermal measurement, the samples were annealed in vacuum overnight at 475 K to minimize any PMMA residue that is left on the sample surface. To obtain the sample's thermal transport properties, one membrane was Joule heated, and heat conduction through the sample raises the temperature of the other membrane. The temperature rise in the two membranes was measured using the two Pt RTs. From the measured Joule heat and membrane temperatures, thermal resistance of the sample was obtained.

First-Principles Density Functional Theory (DFT) Calculation of Thermal Conductivity of MoS2: The DFT calculations were performed by the planewave-based Quantum-Espresso package.^[59] A planewave basis was employed with a cut-off energy of 50 Rydberg and the Monkhorst-Pack^[60] scheme was used to generate an $8 \times 8 \times 1$ k-point mesh. Ultrasoft pseudopotentials with Perdew-Wang 91 generalized gradient approximation^[61] for both Mo and S atoms were applied. Force constant potential was fitted with sets of force-displacement data obtained from DFT calculations. The cutoff of the second and third order force constants are 12.7 and 4.0 Å, respectively. The phonon dispersion relations as well as phonon group velocities and heat capacity were calculated based on the harmonic part of force constants. Three phonon scattering rates were estimated using Fermi's golden rule with the anharmonic part of force constants. At last, the thermal conductivity was calculated based on the iterative solution of the Boltzmann transport equation. For such calculations, the grid size in the first Brillouin zone is $30 \times 30 \times 1$. A thickness of 6.15 Å, which is the interlayer distance of bulk 3D MoS_2 , was used for this calculation to ensure fair comparison with the experimental data.^[62] This first-principles method was employed to predict the thermal conductivity of different crystals with great insight and accuracy.^[63-68]

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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- [1] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, *105*, 136805.
- [2] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.
- [3] H. R. Gutiérrez, N. Perea-López, A. L. Elas, A. Berkdemir, B. Wang, R. Lv, F. López-Uras, V. H. Crespi, H. Terrones, M. Terrones, *Nano Lett.* 2012, 13, 3447.
- [4] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nat. Nanotechnol. 2011, 6, 147.
- [5] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, Nat. Nanotechnol. 2012, 7, 699.
- [6] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Nat. Nanotechnol. 2012, 7, 490.
- [7] M. Buscema, M. Barkelid, V. Zwiller, H. S. van der Zant, G. A. Steele, A. Castellanos-Gomez, *Nano Lett.* 2013, 13, 358.
- [8] Z. Jin, Q. Liao, H. Fang, Z. Liu, W. Liu, Z. Ding, T. Luo, N. Yang, Sci. Rep. 2015, 5, 18342.
- 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.
- [10] Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, T.-W. Lin, *Adv. Mater.* **2012**, *24*, 2320.
- [11] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, J. C. Idrobo, *Nano Lett.* **2013**, *13*, 2615.
- [12] A. M. Van der zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G. H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, J. C. Hone, *Nat. Mater.* **2013**, *12*, 554.
- [13] Z. Lin, B. R. Carvalho, E. Kahn, R. Lv, R. Rao, H. Terrones, M. A. Pimenta, M. Terrones, 2D Mater. 2016, 3, 022002.
- [14] Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, T.-W. Lin, *Adv. Mater.* **2012**, *24*, 2320.



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- [15] H. Qiu, T. Xu, Z. Wang, W. Ren, H. Nan, Z. Ni, Q. Chen, S. Yuan, F. Miao, F. Song, G. Long, Y. Shi, L. Sun, J. Wang, X. Wang, *Nat. Commun.* **2013**, *4*, 2642.
- [16] S. KC, R. C. Longo, R. Addou, R. M. Wallace, K. Cho, Nanotechnology 2014, 25, 375703.
- [17] S. Tongay, J. Suh, C. Ataca, W. Fan, A. Luce, J. S. Kang, J. Liu, C. Ko, R. Raghunathanan, J. Zhou, F. Ogletree, J. Li, J. C. Grossman, J. Wu, *Sci. Rep.* 2013, *3*, 2657.
- [18] P. K. Chow, R. B. Jacobs-Gedrim, J. Gao, T.-M. Lu, B. Yu, H. Terrones, N. Koratkar, ACS Nano 2015, 9, 1520.
- [19] 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.
- [20] H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, A. V. Krasheninnikov, Phys. Rev. Lett. 2012, 109, 035503.
- [21] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, J. Lou, *Nat. Mater.* **2013**, *12*, 754.
- [22] H. Schmidt, S. Wang, L. Chu, M. Toh, R. Kumar, W. Zhao, A. H. C. Neto, J. Martin, S. Adam, B. Ozyilmaz, G. Eda, *Nano Lett.* 2014, 14, 1909.
- [23] R. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A. R. H. Walker, H. G. Xing, ACS Nano 2014, 8, 986.
- [24] A. Taube, J. Judek, A. Lapinśka, M. Zdrojek, ACS Appl. Mater. Interfaces 2015, 7, 5061.
- [25] 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.
- [26] J. J. Bae, H. Y. Jeong, G. H. Han, J. Kim, H. Kim, M. S. Kim, B. H. Moon, S. C. Lim, Y. H. Lee, *Nanoscale* **2017**, *9*, 2541.
- [27] W. Li, J. Carrete, N. Mingo, Appl. Phys. Lett. 2013, 103, 253103.
- [28] X. Gu, R. Yang, Appl. Phys. Lett. 2014, 105, 131903.
- [29] B. Peng, Z. Ning, H. Zhang, H. Shao, Y. Xu, G. Ni, H. J. Zhu, *Phys. Chem. C* 2016, 120, 29324.
- [30] Y. Hong, J. Zhang, X. C. J. Zeng, Phys. Chem. C 2016, 120, 26067.
- [31] Y. Q. Cai, J. H. Lan, G. Zhang, Y. W. Zhang, Phys. Rev. B: Condens. Matter 2014, 89, 035438.
- [32] Z. Ding, Q.-X. Pei, J.-W. Jiang, Y.-W. J. Zhang, Phys. Chem. C 2015, 119, 16358.
- [33] X. Wu, N. Yang, T. Luo, Appl. Phys. Lett. 2015, 107, 191907.
- [34] L. Shi, D. Y. Li, C. H. Yu, W. Y. Jang, D. Kim, Z. Yao, P. Kim, A. Majumdar, J. Heat Transfer 2003, 125, 881.
- [35] A. Mavrokefalos, M. T. Pettes, F. Zhou, L. Shi, *Rev. Sci. Instrum.* 2007, 78, 034901.
- [36] J. Gao, B. Li, J. Tan, P. Chow, T.-M. Lu, N. Koratkar, ACS Nano 2016, 10, 2628.
- [37] M. T. Pettes, I. S. Jo, Z. Yao, L. Shi, Nano Lett. 2011, 11, 1195.
- [38] I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, L. Shi, Nano Lett. 2013, 13, 550.
- [39] I. Jo, M. T. Pettes, E. Ou, W. Wu, L. Shi, Appl. Phys. Lett. 2014, 104, 201902.
- [40] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, ACS Nano 2010, 4, 2695.
- [41] G. Plechinger, J. Mann, E. Preciado, D. Barroso, A. Nguyen, J. Eroms, C. Schuller, L. Bartels, T. Korn, Semicond. Sci. Technol. 2014, 29, 064008.
- [42] W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, R. S. Ruoff, Nano Lett. 2010, 10, 1645.
- [43] S. Chen, A. L. Moore, W. Cai, J. W. Suk, J. An, C. Mishra, C. Amos, C. W. Magnuson, J. Kang, L. Shi, R. S. Ruoff, ACS Nano 2011, 5, 321.
- [44] C. Kittel, Introduction to Solid State Physics, 7th ed., Wiley, New York, USA **1996**.
- [45] X. Gu, R. Yang, Appl. Phys. Lett. 2014, 105, 131903.
- [46] W. Li, J. Carrete, N. Mingo, Appl. Phys. Lett. 2013, 103, 253103.

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- [47] S. Neogi, J. S. Reparaz, L. F. C. Pereira, B. Graczykowski, M. R. Wagner, M. Sledzinska, A. Shchepetov, M. Prunnila, J. Ahopelto, C. M. Sotomayor-Torres, D. Donadio, ACS Nano 2015, 9, 3820.
- [48] G. Li, M. Yarali, A. Cocemasov, S. Baunack, D. L. Nika, V. M. Fomin, S. Singh, T. Gemming, F. Zhu, A. Mavrokefalos, O. G. Schmidt, ACS Nano 2017, 11, 8215.
- [49] S. Bertolazzi, J. Brivio, A. Kis, ACS Nano 2011, 5, 9703.
- [50] M. Sledzinska, B. Graczykowski, M. Placidi, D. Saleta Reig, A. El Sachat, J. S. Reparaz, F. Alzina, B. Mortazavi, R. Quey, L. Colombo, S. Roche, C. M. Sotomayor Torres, 2D Mater. 2016, 3, 035016.
- [51] Z. Wang, J. E. Alaniz, W. Jang, J. E. Garay, C. Dames, Nano Lett. 2011, 11, 2206.
- [52] A. Y. Serov, Z.-Y. Ong, E. Pop, Appl. Phys. Lett. 2013, 102, 033104.
- [53] S.-I. Tamura, Phys. Rev. B 1983, 27, 858.
- [54] N. Mingo, K. Esfarjani, D. A. Broido, D. A. Stewart, Phys. Rev. B. 2010, 81, 045408.
- [55] G. Xie, Y. Shen, X. Wei, L. Yang, H. Xiao, J. Zhong, G. Zhang, Sci. Rep. 2014, 4, 5085.
- [56] D. Saha, S. Mahapatra, J. Appl. Phys. 2016, 119, 134304.
- [57] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hoa, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, R. S. Ruoff, ACS Nano 2011, 5, 6916.

- [58] M. Yarali, J. Hao, M. Khodadadi, H. Brahmi, S. Chen, V. G. Hadjiev, Y. J. Jung, A. Mavrokefalos, RSC Adv. 2017, 7, 14078.
- [59] G. Paolo, B. Stefano, B. Nicola, C. Matteo, C. Roberto, C. Carlo, C. Davide, L. C. Guido, C. Matteo, D. Ismaila, C. Andrea Dal, G. de Stefano, F. Stefano, F. Guido, G. Ralph, G. Uwe, G. Christos, K. Anton, L. Michele, M.-S. Layla, M. Nicola, M. Francesco, M. Riccardo, P. Stefano, P. Alfredo, P. Lorenzo, S. Carlo, S. Sandro, S. Gabriele, P. S. Ari, S. Alexander, U. Paolo, M. W. Renata, J. Phys. Condens. Matter. 2009, 21, 395502.
- [60] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188.
- [61] J. P. Perdew, P. Ziesche, H. Eschrig, *Electronic Structure of Solid*, Akademie Verlag, Berlin **1991**, p. 11.
- [62] X. Wu, V. Varshney, J. Lee, Y. Pang, A. K. Roy, T. Luo, Chem. Phys. Lett. 2017, 669, 233.
- [63] L. Lindsay, D. A. Broido, N. Mingo, Phys. Rev. B 2010, 82, 115427.
- [64] A. Cepellotti, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, N. Marzari, Nat. Commun. 2015, 6, 6400.
- [65] K. Esfarjani, G. Chen, H. T. Stokes, Phys. Rev. B 2011, 84, 085204.
- [66] X. Wu, J. Lee, V. Varshney, J. L. Wohlwend, A. K. Roy, T. Luo, Sci. Rep. 2016, 6, 22504.
- [67] X. Wu, V. Varshney, J. Lee, T. Zhang, J. L. Wohlwend, A. K. Roy, T. Luo, Nano Lett. 2016, 16, 3925.
- [68] Z. Liu, X. Wu, T. Luo, 2D Mater. 2017, 4, 025002.