Phonon and Thermal Properties of Thin Films Made from WS$_2$ Mono- and Few-Layer Flakes

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ABSTRACT: We first report the temperature phonon properties of a large-area thin film (lateral size: ∼mm, thickness ∼50 nm) made from WS$_2$ mono and few layers deposited on the SiO$_2$/Si substrate. We show that temperature phonon properties probed by Raman spectroscopy significantly differ for bulk and thin-film systems in a temperature range of 90−450 K; however, both exhibit strong temperature-dependent phonon energy nonlinear behavior. Employing the optothermal Raman method, we also estimate thin-film thermal conductivity ($\kappa = 4.3$ W/(m K)) and thermal interface conductance ($g = 5.5$ MW/(m$^2$ K)) at room temperature. We find that the thermal properties of thin films ($\kappa$ and $g$) are 1 order of magnitude lower than that for bulk or monolayer WS$_2$, which is caused by a reduction in flake size and an increase in boundary scattering. This finding is important for heat management in future applications of thin films made from two-dimensional (2D) nanoflakes.

1. INTRODUCTION

Tungsten disulfide (WS$_2$) is a layered van der Waals material and a well-known member of the transition-metal dichalcogenides family. In recent years, it has been extensively studied as a future component of electronic devices because of its unique optical and electronic characteristics. The most studied polytype, 2H, is a semiconductor with a tunable direct−indirect band gap between 1.3 and 2.1 eV depending on the number of atomic layers of WS$_2$. A tunable band gap in the visible spectrum with favorable electronic parameters such as mobility or high on/off ratio make WS$_2$ a suitable candidate for various electronic and optoelectronic devices like field-effect transistors or photodetectors.

With a growing demand for better heat management in electronic devices, understanding the phonon properties of new materials becomes increasingly important as they influence the materials’ thermal properties and scattering effects. In the case of tungsten disulfide, temperature-dependent phonon properties and thermal properties of crystalline bulk and monolayer samples were studied previously. For example, the values of in-plane thermal conductivity were found to be 124 W/(m K) for bulk and 32 W/(m K) for a suspended monolayer. Also, phonon properties were only studied considering linear and nonlinear phonon behavior in a large temperature range of 77−543 K for bulk and monolayer WS$_2$. Despite these experimental results, the information about the thermal and phonon properties of a more complex structure like a thin film made from WS$_2$ mono- and few-layered flakes is still missing in the literature.

Thin films made from two-dimensional (2D) flakes are becoming increasingly relevant with an increase in the mass production of nanoflakes-based inks via the liquid exfoliation technique and diverse thin-film production methods like inject printing and vacuum filtration. To date, these technologies were implemented to produce various building blocks of the electronic components and proof-of-concept electronic circuits for flexible electronics. Considering the difference in architecture of bulk and the thin film made from overlapping mono- and few-layer flakes, especially reduction in flake size, the naturally occurring disorder, various strengths of flake−flake interaction, and grain boundaries, the question arises of what effect does the structure of the sample has on the phonon and thermal properties.

In this work, we used commercially available WS$_2$ mono- and few-layer powder to fabricate a thin (∼50 nm) film on the SiO$_2$ substrate to study its phonon and thermal properties. We used Raman spectroscopy to conduct a comparative study of temperature-dependent phonon properties of a thin film made

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from nanoflakes and bulk WS₂. Such measurements can bring new insights into anharmonic crystalline potential, which is crucial for understanding the temperature-dependent thermal properties of materials. We also used the state-of-the-art optothermal Raman technique to estimate for the first time in-plane thermal conductivity (κ) and thermal interface conductance (g) of a thin film made from WS₂ nanoflakes. Both the phonon and thermal properties differ between bulk and thin film with an order of magnitude lower thermal properties of the thin film compared to the bulk sample. We find for thin films 0.21 (3) W/(m K) and 5.5 (6) MW/(m² K). These results deepen the understanding of the phonon and thermal properties of 2D materials and can be used to design better heat management systems in future applications of WS₂ and other 2D nanoflakes thin films.

2. METHODS

WS₂ thin films were prepared by liquid exfoliation and vacuum filtration methods using commercially available monolayer WS₂ powder (ACS Material, monolayer ratio ≥90%, thickness ~1 nm, typical flake diameter: 0.1–4 μm). The structure of the flakes was indeed confirmed by Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The powder was dispersed in isopropanol by the ultrasonication process and filtered through a cellulose membrane. Next, the films were transferred on SiO₂ and glass substrates for Raman and absorption measurements, respectively. These methods produce a large-area (~nm to cm in scale) continuous layer of randomly distributed, overlapping flakes in a complex thin-film system of desired thickness. As bulk WS₂, we used mechanically exfoliated thick flake (~720 nm) on SiO₂ substrate from WS₂ crystal purchased from SPI supplier. All samples were stored in a dark container to avoid photooxidation effects.

Raman measurements were performed using a Renishaw InVia Qntor spectrometer in a backscattering configuration with a motorized XYZ stage that offered 100 nm resolution. All spectra were collected using a 100× long distance objective with the numerical aperture of 0.8, minimum beam radius rₑ = 0.21 μm, circularly polarized light, 514.5 nm (2.41 eV) laser, and 3000 lines/mm grating. Resolution of the Raman system is less than 1 cm⁻¹. Laser power was measured using the Ophir DSC600 optical cell with a temperature resolution of 0.1 K. All measurements were done in an argon atmosphere to exclude photooxidation and possible oxidation at higher temperatures.

Additional characterization was performed using a Bruker Icon atomic force microscope for thickness and topography inspection, a photovoltaic response analyzer PVE300 Bentham for absorption determination, and a Raith e-Line plus electron microscope to obtain SEM images.

3. RESULTS AND DISCUSSION

As a starting point, we discuss basic structural information about studied samples. Figure 1a shows an optical image of the bulk WS₂ sample exfoliated on a 285 nm SiO₂/Si substrate. Flakes with a homogeneous large lateral area and thickness of 724 nm was chosen as a bulk sample. For the thin film, to capture the morphology of the sample, we present an SEM image in Figure 1b. We can see the highly disordered, polycrystalline nature of the WS₂ film with an average lateral flake size of less than 1 μm. The average height of produced thin film was measured to be 52 nm. A typical AFM profile at the substrate-film edge can be seen in the inset of Figure 1b. Raman spectra obtained from bulk and thin-film samples at room temperature with an excitation line of 514.5 nm are presented in Figure 1c. Differences in Raman spectra are characteristic of WS₂ thinning. For example, we can see a change in the relative intensity of the A₁g mode (~420 cm⁻¹) and 2LA mode (~350 cm⁻¹) or the appearance of distinct LO mode from silicon substrate for thin film (~520 cm⁻¹), which indicates the film’s relatively high optical transparency.

To properly assess the temperature-dependent WS₂ phonon evolution, we first take a closer look at the A₁g mode, which is presented in Figure 2. Typical spectra in three different temperatures with fitted Lorentz curves for thin film and bulk are presented in Figure 2a,b. The main difference between these samples is a visible asymmetry in thin-film spectra, which we resolve by adding a second mode for a thin-film sample called A₁g* in this article for convenience. In such a case, the double Lorentz fit is in good agreement with experimental data and we see that the relative intensity of A₁g* to A₁g is decreasing with temperature. The bulk sample is well described by single Lorentzian mode, which suggests that the appearance of a new mode in the thin film is the manifestation of the structure and flake composition of the thin film. In fact, the most probable explanation of A₁g* mode splitting is an assumption that A₁g* comes from monolayer flakes within the thin film and A₁g from multilayer flakes. This hypothesis is supported by information from the WS₂ powder produced used in this study (ACS materials), which claims that the powder is composed of more than 90% monolayers. Moreover, the energy of the A₁g* and A₁g modes at 300 K are 418.4 and 421.1 cm⁻¹ which are typical for monolayer and multilayer flakes, respectively. The intensity ratio of 2LA to A₁g* modes for 514.5 nm excitation laser is 2.2, which also agrees with monolayers’ origin of A₁g* mode. Another less likely explanation of the A₁g* mode appearance can be attributed to the manifestation of a typically silent B₁g Raman mode, which is related mainly to structural disorder.
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commonly referred to as three- and four-phonon processes,
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This formula comes from a second and quartic approximation

\[ \omega(T) = \omega_0 + A \left[ 1 + \frac{2}{x^2} - 1 \right] + B \left[ 1 + \frac{3}{x^2} - 1 \right] \]

where \( x = \hbar \omega_0 / 2 k_b T \), \( y = \hbar \omega_0 / 3 k_b T \), \( \omega_0 \) is the phonon frequency at \( T = 0 \) K, and \( A \) and \( B \) are anharmonic constants. This formula comes from a second and quartic approximation of crystal potential and describes the decay of high-energy phonons to two and three phonons with less energy, which is commonly referred to as three- and four-phonon processes, respectively. More often in the literature, the first-order temperature coefficient is extracted, as it is important for advanced Raman experiments involving, for example, heat dissipation or thermal expansion calculation.\(^{22,23}\) First-order temperature coefficient is extracted by the fitting relation shown below to the linear part of the temperature dependence

\[ \omega(T) = \omega_0 + \chi_T T \]

where \( \omega_0 \) is the phonon frequency at \( T = 0 \) K and \( \chi_T \) is the first-order temperature coefficient. In our study, we fit a linear model to data collected for high temperatures, i.e., between 300 and 450 K. Figure 2c,d shows that the nonlinear Balkanski model (solid lines) well describes data in the whole temperature range. The linear model (dashed line) is a good approximation in the high-temperature range, but for lower temperatures, the discrepancy between the two models is evident.

Figure 3 shows the temperature-dependent measurement for the second most prominent WS\(_2\) Raman peak around 350

\[ \text{Figure 2. Raman spectra around 420 cm}^{-1} \text{ for thin film (a) and bulk (b). Splitting of A_{1g} is observed in the thin-film sample. Green solid lines correspond to fitted Lorentzian functions, and solid blue and orange lines correspond to cumulative fits. (c) Temperature dependence of A_{1g} mode. (d) Temperature dependence of A_{1g} mode for bulk and thin-film samples. Solid lines in (c) and (d) are the result of fitted anharmonic model. Dashed lines correspond to linear model.} \]

\[ \text{Figure 3. Raman spectra around 300 cm}^{-1} \text{ for thin film (a) and bulk (b) WS}_2\text{ sample at } T = 300 \text{ K. Green lines show fitted Lorentzian peaks. Solid blue (a) or orange (b) lines show cumulative fit. (c, d) Temperature dependence of the 2LA mode and the E_1^{2g} mode for thin film (blue) and bulk (orange). Solid lines correspond to the fitted anharmonic model. Dashed lines correspond to the fitted linear model.} \]
**Table 1. Temperature Coefficients for Balkanski and Linear Model for Main Raman Modes in Bulk and Thin-Film Samples**

| Mode | Bulk (90–450 K) | Thin Film (300–450 K) |
|------|-----------------|----------------------|
|      | $\omega_0$ (cm$^{-1}$) | $A$ (cm$^{-1}$) | $B$ (cm$^{-1}$) | $\omega_0$ (cm$^{-1}$) | $\chi_T$ (10$^{-2}$ cm$^{-1}$ K$^{-1}$) |
| $A_{1g}$ ($\Gamma$) | 423.91 (12) | -0.87 (12) | -0.125 (16) | 424.63 (8) | -1.17 (2) |
|      | 424.85 (6) | -1.38 (6) | -0.072 (59) | 425.19 (3) | -1.25 (1) |
| $E_{2g}^*$ | 419.41 (24) | 0.00 (23) | -0.146 (33) | 421.12 (22) | -0.89 (6) |
| $A_{1g}$ | 354.93 (2) | -0.89 (18) | -0.019 (22) | 355.00 (32) | -0.83 (9) |
| $E_{1g}$ ($\Gamma$) | 358.19 (5) | -0.04 (5) | -0.132 (6) | 359.94 (7) | -1.03 (2) |
|      | 359.52 (11) | -0.88 (10) | -0.056 (13) | 360.06 (12) | -1.12 (3) |

Surprisingly, the $A_{1g}^*$ mode can be described only by four-phonon processes, which is an anomalous behavior in phonon temperature studies. To explain this, first, we point out that we observe large relative uncertainty (uncertainty of measurement divided by measured value) of $A$ constant in the $A_{1g}^*$ mode because of the convoluted and asymmetric nature of thin-film Raman peak around 420 cm$^{-1}$. Second, previous works considering the monolayer on a substrate shows that in contrast to our results, the $A_{1g}$ mode can be described only by three-phonon processes. Moreover, the atypical behavior of temperature dependence of the $A_{1g}$ energy for monolayer WS$_2$ can be explained by including thermal expansion. In a thin film made from 2D flakes, the influence of thermal expansion is difficult to describe because of the large number of flakes in the studied system. Because of this, we consciously ignore thermal expansion for a clear comparison between bulk and thin-film samples.

A numerical comparison between our results and other experimentally obtained data is shown in Table S1 in the Supporting Information. We point out that many experimental details and procedures could influence the obtained results, which is why we decided to run a comparative study between bulk and thin films. Despite that, Table S1 shows that first-order linear temperature coefficients are of the same order of magnitude in our work as in other reports. It is interesting that our work shows that the magnitude of first-order coefficients in the linear model decreases when switching from bulk to thin-film sample, which could indicate that the thermal conductivity of the thin-film sample is smaller than the bulk sample.

Now we turn our attention toward the estimation of thermal conductivity and thermal interface conductance of WS$_2$ thin film on SiO$_2$ substrate. To do so, we used the well-established optothermal Raman technique, which studies phonon response to global heating and local laser heating. The details of the experimental and theoretical basis of this method can be found in our previous works and Supporting Information. In brief, during the Raman experiment, we can increase the temperature of the sample by laser illumination. The temperature increase is dependent on power input and distribution. Power can be easily changed by a set of gray filters, and the distribution of power can be modified by changing laser spot size. Assuming our beam has a Gaussian shape, spot size can be changed by moving the sample in and out of the laser focal point as we can easily relate beam radius to distance from the focal point $z_f$. The temperature increase caused by changes in laser power or spot size is observed by softening phonon energy. In the case of WS$_2$ thin film, this effect for average $A_{1g}$ mode position is presented in Figure 4a. To exclude constant error in our measurements, for each value of $z_f$, we take the derivative of the $A_{1g}$ mode position with respect to laser power, which is presented in the inset of Figure 4a. Next, knowing absorption of studied material and how phonon energy changes with temperature, we can experimentally measure temperature increase for given spot size using the following formula

$$ \frac{\partial T}{\partial P_{abs}} \bigg|_{z_f=\text{const}} = \alpha^{-1} \chi_T \chi^{-1} = \alpha^{-1} \frac{\partial \omega}{\partial P} \frac{\partial T}{\partial \omega} $$

(3)

where $\alpha$ indicates absorption (for $\Delta L = 14.5$ nm $\alpha = 28\%$, see Figure S1) and $P$ indicates laser power. The effect of this operation is shown in Figure 4b with blue dots. We note that to conduct optothermal Raman experiment properly, we used one Lorentz for $A_{1g}$ mode fitting, which explains peak position values presented in Figure 4a. For a detailed explanation of this step, see Figure S1 in the Supporting Information. Moreover, to take into account the inhomogeneity of the thin film and collect a representative set of Raman data, we repeat power and spot size dependence measurement 30 times in different spots on the sample and average collected results (see Figure S2).

The measured temperature increase is connected to the ability of heat dissipation within the sample. In the case of a thin film on substrate, heat dissipation depends almost entirely...
on in-plane thermal conductivity $\kappa$ and thermal interface conductance $g$ between WS$_2$ film and SiO$_2$ substrate. To simulate temperature increase in the studied system, one can solve a set of differential equations describing heat dissipation in these layers caused by the absorption of laser illumination. By fitting the simulated curve of temperature increase to experimental data from Figure 4b, we find that $\kappa = 4.3 \pm 3$ W/(m K) and $g = 5.5 \pm 6$ (m K)/W. A good agreement between simulation and experimental data is achieved, which can be seen in Figure 4b. The obtained results confirmed our assumption that the thermal conductivity of such a film is lower than bulk. Both $\kappa$ and $g$ are at least 1 order of magnitude lower than single-crystalline mono- and bulk WS$_2$ (see Table 2). This result can be explained considering lateral flake size and mean free path of phonons, which are dominant heat carriers in WS$_2$. The main contribution to the thermal conductivity of WS$_2$ comes from phonons with a mean free path between 0.1 and 1 $\mu$m; therefore, in thin film with average flake size less than 1 $\mu$m, one should expect a reduction of thermal conductivity. Except flake size, attachment and interaction between overlapping flakes increase phonon boundary scattering, which also should play an important role in limiting in-plane heat conduction. Moreover, weaker interaction between film and substrate caused mainly by a more porous structure at the interface, which reduces the surface area in contact with the substrate, can also explain a lower value of thermal boundary conductance compared to a CVD sample. We also remind that for WS$_2$, as for low-doped semiconductors, phonons are the main heat carriers, which makes a correlation between change in phonon and change in thermal properties more prominent. In the end, we point out that results presented here are part of a larger trend as similar results were shown for graphene and MoS$_2$, where the films produced from nanoflakes have also at least 1 order of magnitude smaller thermal conductivity than their monocrystalline bulk and monolayer counterparts (see Table 2). Such results can be useful in managing the heat in future applications of thin film and bring new insights into proper device optimization and design.

4. CONCLUSIONS

In summary, we performed a comparative study of temperatures phonon properties of bulk WS$_2$ and thin film made from mono- and few layers. The differences in temperature phonon response in bulk and thin film are related to the differences in structure between the samples. These manifest in the thin film with a greater significance of four-phonon processes and lower values of first-order temperature coefficients for all Raman modes. We also estimated the thermal conductivity and thermal interface conductance to SiO$_2$ for the thin film made from mono- and few layers. We found $\kappa = 4.3 \pm 3$ W/(m K) and $g = 5.5 \pm 6$ (m K)/W. Measured values are 1 order of magnitude lower than single-crystalline mono- and bulk WS$_2$. These results enriched the understanding of the thermal properties of the thin films made from 2D materials and can be used for better heat management in future applications of such films.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02842.

Detailed theoretical description of the optothermal Raman method; additional experimental results for optothermal Raman experiment for the WS$_2$ thin film; and summary of anharmonic constants and first-order temperature coefficients for WS$_2$ samples found in the literature (PDF).

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