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Temperature-Dependent Phonon Shifts in Mono-layer, Few-layer, and Bulk WS₂ Films

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Abstract: Two-dimensional transition metal disulfides (TMDs) have recently attracted significant research attention due to their rich physical and chemical properties. Graphene has also been studied intensively due to its high electron mobility of $\sim 200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. Since there is no band gap, it is difficult for a graphene-based device to achieve high current on/off ratio. For TMDs, such as MoS₂, MoSe₂, WSe₂, and WS₂, the band gaps of these materials can be adjusted according to the number of layers. Since TMD has the advantage of suppressing source-drain tunneling current in an ultra-short transistor and offering superior immunity to short-channel effects, it is also attractive for use as a channel material in Si complementary metal oxide semiconductor (CMOS) devices larger than 22 nm. Among them, MoS₂ in single-layer and multi-layer films have been intensively researched for many years. MoS₂-based field effect transistors (FETs) with excellent electrical properties have been reported. WS₂ has lower in-plane electronic mass than MoS₂, MoSe₂, and MoTe₂, and therefore has potential for higher carrier mobility or higher output current for WS₂-based FETs. Experimental research on WS₂ is limited compared to MoS₂, and more work is needed to further exploit the full potential of WS₂-based FETs. Therefore, the electron-phonon interaction and vibration properties of WS₂ used in nano-electronic applications and FETs must be investigated. To this end, mono-layer (1L), few-layer (FL), and bulk WS₂ films were prepared using mechanical exfoliation from a WS₂ crystal. 3M scotch-tape was used for transferring the WS₂ films. Detailed temperature-dependent Raman study on 1L, FL, and bulk WS₂ films has been conducted using a 514-nm excitation laser. Raman spectroscopy, as an effective and non-destructive approach for phonon vibration study, has been used to evaluate TMDs. The Raman spectra reveal much useful information on the test sample in terms of peak position and spectral shape change. With the film thickness increasing to bulk, the $A_{1g}(\Gamma)$ and $E_{2g}^1(\Gamma)$ modes show blue-shift and red-shift, respectively, with respect to 1L WS₂. Moreover, when the dominant Raman vibration modes swaps between $E_{2g}^1(\Gamma)$ and $A_{1g}(\Gamma)$, the “cross-over” temperature was identified for 1L, FL, and bulk WS₂ films. WS₂ shows smaller frequency change Δ between the $E_{2g}^1(\Gamma)$ and $A_{1g}(\Gamma)$ modes than MoS₂, with varying film thickness. The temperature coefficient of the Raman peak position was one magnitude lower for WS₂ than MoS₂, implying that WS₂ has better thermal stability than MoS₂. The results of this systematic study provide a physical guidance for WS₂-based device design.

Key Words: WS₂; Film thickness; Raman; Photoluminescence; Vibration mode

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单层, 少层和块状 WS₂ 薄膜中声子位移随温度的变化

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摘要: 近年来, 二维过渡金属二硫化物(TMD)由于其良好的物理和化学性质而引起人们的关注。其中, 石墨烯由于其高达 $200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ 高电子迁移率得到了深入研究。由于石墨烯没有带隙, 因此基于石墨烯的器件难以实现高的电流开关比。对于二维过渡金属二硫化物例如 MoS₂、MoSe₂、WSe₂ 和 WS₂, 这些材料可以根据层数来调节的带隙。其中, 单层和多层 MoS₂ 薄膜已进行了广泛深入研究。已经有人实现具有优异电学性能的基于 MoS₂ 的场效应晶体管(FET)。与 MoS₂、MoSe₂ 和 MoTe₂ 相比, WS₂ 具有更低的面内电子质量, 这表明基于 WS₂ 的 FET 具有更高的载流子迁移率或更高的输出电流。与 MoS₂ 相比, WS₂ 缺乏系统的研究, 需要更多的研究工作来进一步发掘基于 WS₂ 的场效应晶体管的潜能。因此, 我们使用机械剥离法来制备 WS₂ 晶体单层(1L), 少层(FL)和块状 WS₂ 薄膜。使用 3M 透明胶带转移 WS₂ 薄膜, 并且使用 514 nm 激光器对 1L、FL 和块状 WS₂ 膜进行了变温的拉曼研究。随着膜厚度增加到块状, 对于 1L WS₂, A_{1g}(Γ) 和 E_{2g}(Γ) 模式分别显示蓝移和红移。此外, 当拉曼振动模式在 E_{2g}(Γ) 和 A_{1g}(Γ) 之间交换时, “交叉” 温度被识别为 1L、FL 和块状 WS₂ 膜。与 MoS₂ 相比, 随着膜厚度的变化, WS₂ 在 E_{2g}(Γ) 和 A_{1g}(Γ) 之间表现出较小的频率变化(Δ), 并且从拉曼峰值位置随温度变化来看, WS₂ 比 MoS₂ 少一个量级。这项作为基于 WS₂ 的器件设计提供了物理指导。

关键词: 二硫化钨; 薄膜厚度; 拉曼; 光致发光; 振动模式
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1 Introduction

Two-dimensional transition metal dichalcogenides (TMDs) have recently gained much interest due to their rich physical and chemical properties, which enable the future applications in nano-electronics^{1,2}, nano-photonics³⁻⁵, and valley-electronics⁶⁻⁸. The counterpart graphene, has also been intensively investigated due to its high electron mobility $\sim 200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, since its first mechanical exfoliation by Novoselov *et al.* in 2004^{9,10}. However, due to its absence of bandgap, to achieve high current on/off ratio is difficult for graphene-based devices. Several techniques have been proposed to create the bandgap for graphene. For example, employing quantum mechanical confinement in patterned¹¹ or exfoliated graphene nano-ribbons¹² introduces a bandgap up to 400 meV, and applying perpendicular electric field (voltage exceeding 100 V) in bi-layer graphene creates a bandgap up to 250 meV¹³. These innovative methods of introducing a bandgap in graphene always come with a price of significant mobility degradation ($\sim 200 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), process complexity, or device reliability under high voltage¹⁴⁻¹⁶. For TMDs, such as MoS₂, MoSe₂, WSe₂, and WS₂ etc, these materials have a bandgap, which is tunable based on the number of layer. Usually, the bandgap of the bulk TMDs is $\sim 1.2\text{--}1.3 \text{ eV}$, and one of mono-layer TMDs is $\sim 1.8\text{--}2.1 \text{ eV}$, the increase of bandgap with decreasing number of layer for TMDs is due to the carrier quantum confinement at an atomic scale. Being able to achieve atomic thickness and have a bandgap larger than that of silicon, TMDs are also attractive for being used as the channel material for Si CMOS devices beyond sub-22 nm, since TMDs have advantage for suppressing the source-to-drain tunneling

current in ultra-short transistors and offering superior immunity to short-channel effects¹⁷.

Among TMD group, MoS₂ in both mono- and few-layer films has been intensively studied in the research community over the years¹⁸⁻²³. MoS₂-based field effect transistors (FETs) with excellent electrical characteristics have been demonstrated, such as high current on/off ratio ($\sim 10^8$), low subthreshold swing ($\sim 70\text{--}80 \text{ mV} \cdot \text{dec}^{-1}$), mobility up to $\sim 200 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (in high-*k*/MoS₂/high-*k* structure)²⁴. As a typical TMD, WS₂ has been widely used due to its potential excellent performance²⁵. Similar to MoS₂, WS₂ can also be grown through chemical vapor deposition (CVD)²⁶. According to the simulation work by Liu *et al.*²⁷, WS₂ have a lower in-plane electronic mass, compared with MoS₂, MoSe₂, and MoTe₂, which shows the potential for higher carrier mobility or higher output current for WS₂-based FETs. However, as compared with MoS₂, the experimental studies on WS₂ are limited, or more work is required to be done for further harnessing the full potential of WS₂-based FETs. In the literature, mono- and multi-layer WS₂-based FETs were demonstrated, and achieved on/off current ratio of $\sim 10^6\text{--}10^8$ with mobility of $\sim 140\text{--}234 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ²⁸⁻³⁰.

As for the nano-electronic application, it is important to investigate the electron-phonon interaction and vibration properties of WS₂. Raman spectroscopy, as an effective and non-destructive approach for phonon vibration study, has been used to evaluate graphene, and TMDs³¹⁻³³. Raman spectra reveal much useful information of the test sample through Raman peak position and Raman shape change. Temperature dependent phonon shifts of single layer WS₂ by mechanical exfoliation³⁴

and multi-layer WS₂ by hydrothermal method³⁵, have been investigated by Raman spectroscopy. In this work, we present thickness- and temperature-dependent studies of the phonon vibration mode for mono-layer, few-layer, and bulk WS₂ films prepared by mechanical exfoliation.

2 Experimental

The mono-layer (1L), few-layer (FL), and bulk WS₂ films were prepared on 300 nm SiO₂/Si wafer by mechanical exfoliation from bulk WS₂ crystal, which was purchased from 2D Semiconductor Inc. 3M scotch-tape was used for transferring the WS₂ films. Raman and photoluminescence (PL) spectra were collected in a Renishaw inVia confocal system in the backscattering configuration. The wavelength of the laser was 514 nm (2.4 eV) from an argon ion laser, the grating of 2400 grooves·mm⁻¹ was used to obtain more details of line shapes of the Raman band. The laser power on the sample was set at around 1.0 μW to avoid laser induced heating. The application of a 100× objective lens with a numerical aperture of 0.9 can provide us a spot size of ~1 μm, and spectral resolution was 1 cm⁻¹. The Si peak at 520 cm⁻¹ was used as a reference for wavelength calibration. Atomic force microscopy (AFM) images were obtained under tapping mode using Bruker Dimension Icon.

3 Results and Discussion

The atomic force microscopy (AFM) images of 1L, FL, and bulk WS₂ films are shown in Fig. 1a, b, and c. The film thickness was directly measured by AFM in a non-contact mode. As shown in Fig. 1d, e, and f, the step height or thickness of 1L, FL, and

bulk WS₂ films were measured to be 0.98, 10, and 76 nm. Based on the reported mono-layer WS₂ thickness of ~0.9 nm, the number of layer for 0.98, 10, and 76 nm is determined to be 1L, ~11 L, and ~84 L, respectively. In Fig. 2, PL spectra were measured using a 514 nm excitation laser. It is known that the bulk WS₂ is an indirect bandgap semiconductor with a ~1.3 eV bandgap, whereas 1L WS₂ has a direct bandgap of ~2.1 eV. For the bulk WS₂, the electron states involved in the indirect transition (the valence band maximum at Γ point and the conduction band minimum at T point) originate from linear combination of tungsten d -orbital and sulfur p_z -orbital, and their dispersion strongly depends on the number of layers. For the 1L WS₂, the electron states involved in the direct transition (the valence band maximum at K point and the conduction band minimum at K point) mainly originate tungsten d -orbital, and their energies are not very sensitive to the number of layers³⁶. In Fig. 2, one sharp PL peak centered at ~638.5 nm is observed for 1L WS₂ and the measured spectral range nearly vanishes for the FL WS₂ sample. When the thickness decreases to 1L, the dramatic increase of the PL intensity is a signature of the transformation from indirect to direct bandgap structures. Based on the PL peak for 1L WS₂ shown in Fig. 2, the bandgap of 1L WS₂ is estimated from the PL peak to be ~1.94 eV, which is smaller than ~2.1 eV. Direct electronic transitions in 1L WS₂ originate from excitonic radiative relaxation, and for this reason the PL peak signal always appears at energies slightly lower than ~2.1 eV direct bandgap of WS₂.

Raman studies of 1L, FL, and bulk WS₂ films have been carried out using a 514 nm excitation laser, since Raman spectrum of WS₂ under a 514 nm excitation laser becomes very

Fig. 1 The atomic force microscopy (AFM) images of (a) 1L, (b) FL, and (c) bulk WS₂ films. The step height or thickness of (d) 1L, (e) FL, and (f) bulk WS₂ films.

Fig. 2 Photoluminescence spectra from FL to 1L. One sharp PL peak centered at ~638.5 nm for 1L WS₂, however nearly no peak for the FL sample.

rich, revealing many second-order peaks^{37,38}. Raman spectra at 300 K of 1L, FL, and bulk WS₂ films are shown in Fig. 3a, b, and c. Raman active modes of WS₂ comprise of A_{1g} , E_{1g} , E_{2g}^1 , and E_{2g}^2 at the center of the Brillouin zone, but E_{1g} is forbidden in the back-scattering configuration and E_{2g}^2 is less studied due to its low frequency out of the most conventional Raman spectral range. The A_{1g} mode is related to the out-of-plane vibration of sulfur atoms, and the E_{2g}^1 mode is associated with the in-plane vibration of tungsten and sulfur atoms. Under a 514 nm excitation laser, the $A_{1g}(I)$ mode was observed at 419 cm⁻¹ and dominant $2LA(M)$ mode observed at ~350 cm⁻¹ overlapping with $E_{2g}^1(I)$ mode (~355 cm⁻¹), which was acquired by multi-Lorentzian fitting. Fig. 3d, e, and f show the multi-Lorentzian fitting of $2LA(M)-2E_{2g}^2(I)$, $E_{1g}(M)$, $2LA(M)$, and $E_{2g}^1(I)$ modes for 1L, FL, and bulk WS₂ films, respectively. When the number of layer increases from 1L to bulk, the $A_{1g}(I)$ mode shows a blue-shift of 1.34 cm⁻¹ from 419.14 to 420.48 cm⁻¹, similar to the trend observed for MoS₂, as the van der Waals interactions between the layers increase the restoring force in the thicker layers. On the other hand, $E_{2g}^1(I)$ mode shows a red-shift of 0.69 cm⁻¹ from 354.59 (1L) to 353.90 cm⁻¹ (bulk), which is attributed to the increment of dielectric long-range coulomb interactions among the effective charges. It is worth noting that in WS₂, the close proximity of the $2LA(M)$ and $E_{2g}^1(I)$ modes increases the error in determining the frequency shift. As compared with MoS₂, the $A_{1g}(I)$ blue-shift of 1.34 cm⁻¹ and the $E_{2g}^1(I)$ red-shift of 0.69 cm⁻¹ of WS₂ are much smaller, as the A_{1g} blue-shift and the E_{2g}^1 red-shift of MoS₂ as increasing 1L to bulk is ~4.2 and 2.2 cm⁻¹, respectively. As shown in Fig. 3, the frequency difference (Δ) between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes is varied from 64.55 to 66.58 cm⁻¹, when the number of WS₂ layer increases from 1L to bulk. The Δ between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes for 1L WS₂ prepared by mechanical exfoliation is reported to be 64 cm⁻¹ by Thirupuranthaka *et al.*³⁴. In the literature, Δ between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes is also increased from ~62 to 65 cm⁻¹, when the number of WS₂ layer increases from 1L to bulk prepared by chemical vapor deposition (CVD) method. Although this observed trend is similar to that of MoS₂, there are a larger Δ

change between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes (from ~19 to ~25 cm⁻¹), when the number of MoS₂ layer increases from 1L to bulk. It is noted that the Δ (~18 cm⁻¹) between A_{1g} and E_{2g}^1 modes for the 1L MoS₂ by mechanical exfoliation is smaller than that of 1L MoS₂ by CVD method (~19 cm⁻¹). However, based on the reported values in the literature, the case for WS₂ is opposite, since the Δ (~64 cm⁻¹) between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes for the 1L WS₂ by mechanical exfoliation is larger than that (~62 cm⁻¹) of 1L WS₂ by CVD method. Further, it looks that Raman vibration mode for WS₂ is less sensitive to the number of layer as compared to MoS₂. Δ between A_{1g} and E_{2g}^1 modes is often used to identify the number of layer in MoS₂ films. Due to the less sensitivity of Δ between $A_{1g}(I)$ and $E_{2g}^1(I)$ modes to the number of layer for WS₂, more accurate or robust method is needed for identifying the number of layer in WS₂ films, except for the AFM direct measurement method.

Temperature-dependent Raman measurements of 1L, FL, and bulk WS₂ films have been carried out at 80–300 K under a 514 nm excitation laser, and the results are shown in Fig. 4a, b, and c. In this part, we will focus on the discussion about peak intensity ratio [$2LA(M)/A_{1g}(I)$, $E_{2g}^1(I)/A_{1g}(I)$, etc.] and peak position as a function of temperature. In viewing of WS₂ as the potential CMOS channel material beyond Si, it is important to study the electron-phonon interactions or vibration modes under various temperatures through non-destructive Raman method. The temperature-dependent Raman vibration modes of WS₂ can have a direct bearing on the carrier transport of WS₂-based FETs. As shown in Fig. 5, the $2LA(M)/A_{1g}(I)$, $E_{2g}^1(I)/A_{1g}(I)$, and Rec. [$2LA(M)$, $E_{2g}^1(I)$]/ $A_{1g}(I)$ peak intensity ratio are plotted as a function of temperature for (a) 1L, (b) FL, and (c) bulk WS₂. Rec. [$2LA(M)$, $E_{2g}^1(I)$] is the recombination of $2LA(M)$ and $E_{2g}^1(I)$ modes, or the mode without multi-Lorentzian fitting. The peak intensity of Rec. [$2LA(M)$, $E_{2g}^1(I)$], $2LA(M)$, $E_{2g}^1(I)$, and $A_{1g}(I)$ as a function of temperature for 1L, FL, and bulk WS₂ films can be referred to Fig. 5. With the temperature decreasing,

Fig. 3 Raman spectra at 300 K of (a) 1L, (b) FL, and (c) bulk WS₂ film under a 514 nm excitation laser. Multi-Lorentzian fitting of $2LA(M)-2E_{2g}^2(I)$, $E_{1g}(M)$, $2LA(M)$, and $E_{2g}^1(I)$ modes for (d) 1L, (e) FL, and (f) bulk WS₂ film, respectively.

Fig. 4 Temperature-dependent Raman measurements of (a) 1L, (b) FL, and (c) bulk WS₂ films at 80–300 K under a 514 nm excitation laser.

Fig. 5 $2LA(M)/A_{1g}(I)$, $E_{2g}(I)/A_{1g}(I)$, and $\text{Rec.}[2LA(M), E_{2g}(I)]/A_{1g}(I)$ peak intensity ratios as a function of temperature for (a) 1L, (b) FL, and (c) bulk WS₂ films.

It is noted that the $\text{Rec.}[2LA(M), E_{2g}(I)]/A_{1g}(I)$ ratio is creased to more than 1 at 230, 190, and 160 K, respectively, for 1L, FL, and bulk WS₂ films.

the Raman intensities of $\text{Rec.}[2LA(M), E_{2g}(I)]$, $2LA(M)$, $E_{2g}(I)$, and $A_{1g}(I)$ are increasing at different rates for 1L, FL, and bulk WS₂ films. As shown in Fig. 5, it is noted that the $\text{Rec.}[2LA(M), E_{2g}(I)]/A_{1g}(I)$ intensity ratio is creased to more than 1 at 230, 190, and 160 K, respectively, for 1L, FL, and bulk WS₂ films. The $A_{1g}(I)$ vibration mode, related to the out-of-plane vibration of sulfur atoms, is dominated when the temperature is above the “cross-over” point or intensity ratio more than 1; $\text{Rec.}[2LA(M), E_{2g}(I)]$ mode, related to film disorder and in-plane vibration of tungsten and sulfur atoms, is dominated when the temperature is below “cross-over” point or intensity ratio less than 1. The “cross-over” phenomenon is mainly caused by the fast increasing intensity of $2LA(M)$ mode as the temperature decreasing. Based on the “cross-over” temperature, it may be possible to determine the layer number of WS₂ films, since it shows layer-dependent behavior, although more detailed work is needed.

When the temperature decreasing from 300 to 80 K, all the Raman modes of $2LA(M)$, $E_{2g}(I)$, $A_{1g}(I)$, and $A_{1g}(M) + LA(M)$ for 1L, FL, and bulk WS₂ films change linearly as a function of temperature, shown in Fig. 6a, b, c, and d. It is well-known that Raman spectroscopy is a photon-phonon process which is dominant over thermal expansion, as well as the phonon process on the Raman mode linearly shifts with change in temperature. A few data point dispersion for the Raman peak position can be

expected and is well-understood due to the slight variation in the laser spot on the sample, or the local Raman stage vibration, or low excitation power on the sample followed by the extra attenuation from the cold-hot cell window during the measurement. The observed data of peak position obtained from Lorentzian fitting for $2LA(M)$, $E_{2g}(I)$, $A_{1g}(I)$, and $A_{1g}(M) + LA(M)$ modes *versus* temperature were fitted using the Grüneisen model: $\omega(T) = \omega_0 + XT$, where ω_0 is the Raman mode peak position at zero Kelvin temperature, and X is the first-order temperature coefficient of the same mode. The slope of fitted lines gives the first-order temperature coefficient of the specific Raman mode, and shown as an inset in Fig. 6. X values of $2LA(M)$, $E_{2g}(I)$, and $A_{1g}(I)$ modes for the 1L WS₂ are larger than those of FL and bulk WS₂, shown in Fig. 6a, b, and c. However, X ($\sim -0.010 \text{ cm}^{-1} \cdot \text{K}^{-1}$) of $A_{1g}(M) + LA(M)$ mode is almost identical for 1L, FL, and bulk WS₂. Table 1 summarizes the extracted first-order temperature coefficient of $LA(M)$, $2LA(M) - 2E_{2g}(I)$, $E_{2g}(M)$, $2LA(M)$, $E_{2g}(I)$, $A_{1g}(I)$, and $A_{1g}(M) + LA(M)$, for 1L, FL, and bulk WS₂. The X values for the $2LA(M)$, $A_{1g}(I)$, and $A_{1g}(M) + LA(M)$ modes of 1L WS₂ in this work were observed to be close or nearly same as the reported one by Thirupuranthaka *et al.*³⁴. The X variation of $E_{2g}(I)$ between this work and Ref.³⁴ could be due to the error caused by multi-Lorentzian fitting. Also, the reported X for $E_{2g}(I)$ and $A_{1g}(I)$ modes of 1L WS₂ grown by CVD method is -0.0125 and

Fig. 6 Effect of temperature variation on the Raman modes of (a) $2LA(M)$, (b) $E_{2g}^1(I)$, (c) $A_{1g}(I)$, and (d) $A_{1g}(M) + LA(M)$ for 1L, FL, and bulk WS_2 films.

Table 1 Extracted temperature coefficient X for 1L, FL, and bulk WS_2 films.

1L WS_2	$X/(cm^{-1} \cdot K^{-1})$	FL WS_2	$X/(cm^{-1} \cdot K^{-1})$	Bulk WS_2	$X/(cm^{-1} \cdot K^{-1})$
LA(M)	-0.0090	LA(M)	-0.0025	LA(M)	-0.0041
$2LA(M) - 2E_{2g}^1(I)$	-0.0039	$2LA(M) - 2E_{2g}^1(I)$	-0.0001	$2LA(M) - 2E_{2g}^1(I)$	-0.0001
$E_{2g}^1(M)$	-0.0047	$E_{2g}^1(M)$	-0.0010	$E_{2g}^1(M)$	-0.0008
$2LA(M)$	-0.0071	$2LA(M)$	-0.0038	$2LA(M)$	-0.0042
$E_{2g}^1(I)$	-0.0031	$E_{2g}^1(I)$	-0.0016	$E_{2g}^1(I)$	-0.0017
$A_{1g}(I)$	-0.0052	$A_{1g}(I)$	-0.0028	$A_{1g}(I)$	-0.0048
$A_{1g}(M) + LA(M)$	-0.0107	$A_{1g}(M) + LA(M)$	-0.0108	$A_{1g}(M) + LA(M)$	-0.0120

$-0.0149 \text{ cm}^{-1} \cdot \text{K}^{-1}$, respectively, which is larger or one order magnitude higher than the ones reported in this work and Ref. ³⁴. In addition, the reported X for E_{2g}^1 and A_{1g} modes of 1L MoS_2 by mechanical exfoliation method, is ~ -0.017 and $\sim -0.013 \text{ cm}^{-1} \cdot \text{K}^{-1}$, respectively, which is larger or one order magnitude higher than the ones reported in this work and Ref. ³⁹⁻⁴¹. This indicates that the thermal stability of WS_2 may be better than that of MoS_2 , based on the first-order temperature coefficient of the Raman modes. As compared to X ($\sim -0.0162 \text{ cm}^{-1} \cdot \text{K}^{-1}$) of G peak for 1L graphene by mechanical exfoliation, X of 1L WS_2 in this work is also about one order magnitude lower. With the combination of lower in-plan electronic mass and higher thermal stability (or lower temperature coefficient) ⁴², WS_2 could serve as a better candidate for Si CMOS channel material beyond sub-22 nm, as compared to other TMDs. By now, temperature-dependent Raman studies have not been carried out for FL and bulk WS_2 films by mechanical exfoliation in the literature. The presence of substrate 300 nm SiO_2/Si in this work may not affect the final results of temperature coefficient a lot. The effect of

substrate on temperature coefficient of WS_2 grown by CVD has been investigated by Peimyoo *et al.* ³⁹, and only gives about 6% variation. It is interesting to note that we did not observe the dependence of FWHM on the temperature in the examined temperature range in the 1L, FL, and bulk WS_2 samples. This is in contrast with the A_{1g} FWHM temperature dependent for MoS_2 . Further, the variation in the Raman peak position as a function of temperature for the 1L, FL, and bulk WS_2 samples is due to the temperature contribution that consequences from anharmonicity and contribution from the thermal expansion or volume contribution.

4 Conclusions

We have systematically investigated the thickness- and temperature-dependent Raman studies of the phonon vibration mode for mono-layer (1L), few-layer (FL), and bulk WS_2 films prepared by mechanical exfoliation. With the film thickness increasing to bulk, $A_{1g}(I)$ and $E_{2g}^1(I)$ modes show blue-shift of 1.34 cm^{-1} and red-shift of 0.69 cm^{-1} , respectively, with respect

to 1L WS₂. With temperature decreasing, all the Raman peak positions shift to a higher energy. The “cross-over” temperature, when the dominant Raman vibration modes swaps between $E_{2g}^1(I)$ and $A_{1g}(I)$, was identified to be 230, 190, and 160 K, respectively, for 1L, FL, and bulk WS₂ films. As compared to MoS₂, WS₂ shows much smaller frequency change (64.55–66.58 cm⁻¹) between $E_{2g}^1(I)$ and $A_{1g}(I)$ as the film thickness varying, and one magnitude lower temperature coefficient of Raman peak position or better thermal stability. Through this systematic study, the results shown here provide a physical guidance for WS₂-based device engineering.

References

- (1) Ramakrishna Matte, H. S. S.; Gomathi, A.; Manna, A. K.; Late, D. J.; Datta, R.; Pati, S. K.; Rao, C. N. R. *Angew. Chem. Int. Edit.* **2010**, *49* (24), 4059. doi: 10.1002/anie.201000009
- (2) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. *Nat. Nanotech.* **2012**, *7*, 699. doi: 10.1038/nnano.2012.193
- (3) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102* (30), 10451. doi: 10.1073/pnas.0502848102
- (4) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. *Nat. Chem.* **2013**, *5*, 263. doi: 10.1038/nchem.1589
- (5) Perea-López, N.; Elías, A. L.; Berkdemir, A.; Castro-Beltrán, A.; Gutiérrez, H. R.; Feng, S.; Lv, R.; Hayashi, T.; López-Urías, F.; Ghosh, S.; *et al.* *Adv. Funct. Mater.* **2013**, *23* (44), 5511. doi: 10.1002/adfm.201300760
- (6) Mak K F, He K, Shan J, Heinz T F. *Nat. Nanotech.* **2012**, *7*, 494. doi: 10.1038/nnano.2012.96
- (7) Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. *Nat. Nanotech.* **2012**, *7*, 490. doi: 10.1038/nnano.2012.95
- (8) Wu, S.; Ross, J. S.; Liu, G. B.; Aivazian, G.; Jones, A.; Fei, Z.; Zhu, W.; Xiao, D.; Yao, W.; Cobden, D.; *et al.* *Nat. Phys.* **2013**, *9*, 149. doi: 10.1038/nphys2524
- (9) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306* (5696), 666. doi: 10.1126/science.1102896
- (10) Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. *Solid State Commun.* **2008**, *146* (9), 351. doi: 10.1016/j.ssc.2008.02.024
- (11) Han, M. Y.; Özyilmaz, B.; Zhang, Y.; Kim, P. *Phys. Rev. Lett.* **2007**, *98* (20), 206805. doi: 10.1103/PhysRevLett.98.206805
- (12) Li, X.; Wang, X.; Zhang, L.; Lee, S.; Dai, H. *Science* **2008**, *319* (5867), 1229. doi: 10.1126/science.1150878
- (13) Zhang, Y.; Tang, T. T.; Girit, C.; Hao, Z.; Martin, M. C.; Zettl, A.; Crommie, M. F.; Shen, Y. R.; Wang, F. *Nature* **2009**, *459*, 820. doi: 10.1038/nature08105
- (14) Jiao, L.; Zhang, L.; Wang, X.; Diankov, G.; Dai, H. *Nature* **2009**, *458*, 877. doi: 10.1038/nature07919
- (15) Sols, F.; Guinea, F.; Neto, A. H. C. *Phys. Rev. Lett.* **2007**, *99* (16), 166803. doi: 10.1103/PhysRevLett.99.166803
- (16) Yoon, Y.; Guo, J. *Appl. Phys. Lett.* **2007**, *91* (7), 073103. doi: 10.1063/1.2769764
- (17) Cheng, R.; Jiang, S.; Chen, Y.; Liu, Y.; Weiss, N.; Cheng, H. C.; Wu, H.; Huang, Y.; Duan, X. *Nat. Commun.* **2014**, *5*, 5143. doi: 10.1038/ncomms6143
- (18) Yoon, Y.; Ganapathi, K.; Salahuddin, S. *Nano Lett.* **2011**, *11* (9), 3768. doi: 10.1021/nl2018178
- (19) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. *Nat. Nanotech.* **2011**, *6*, 147. doi: 10.1038/nnano.2010.279
- (20) Radisavljevic, B.; Kis, A. *Nat. Mater.* **2013**, *12*, 815. doi: 10.1038/nmat3687
- (21) Schmidt, H.; Wang, S.; Chu, L.; Toh, M.; Kumar, R.; Zhao, W.; Castro Neto, A. H.; Martin, J.; Adam, S.; Özyilmaz, B. *Eda G. Nano Lett.* **2014**, *14* (4), 1909. doi: 10.1021/nl4046922
- (22) Ghatak, S.; Pal, A. N.; Ghosh, A. *ACS Nano* **2011**, *5* (10), 7707. doi: 10.1021/nn202852j
- (23) Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I.; *et al.* *Nat. Mater.* **2014**, *13*, 1135. doi: 10.1038/nmat4091
- (24) Das, S.; Chen, H. Y.; Penumatcha, A. V.; Appenzeller, J. *Nano Lett.* **2013**, *13* (1), 100. doi: 10.1021/nl303583v
- (25) Bikorimana, S.; Lama, P.; Walser, A.; Dorsinville, R.; Anghel, S.; Mitiglu, A.; Micu, A.; Kulyuk, L. *Opt. Express* **2016**, *24* (18), 20685. doi: 10.1364/OE.24.020685
- (26) Gu, H.; Chen, L.; Lu, Y.; Tian, F.; Zhang, Z.; Xu, K.; Wu, J.; Divakar, V. B.; Li, K.; Liu, L. *Jpn. J. Appl. Phys.* **2018**, *57* (6), 060309. doi: 10.7567/JJAP.57.060309
- (27) Liu, L.; Kumar, S. B.; Ouyang, Y.; Guo, J. *IEEE T. Electron Dev.* **2011**, *58* (9), 3042. doi: 10.1109/TED.2011.2159221
- (28) Ovchinnikov, D.; Allain, A.; Huang, Y. S.; Duncenco, D.; Kis, A. *ACS Nano* **2014**, *8* (8), 8174. doi: 10.1021/nn502362b
- (29) Liu, X.; Hu, J.; Yue, C.; Della Fera, N.; Ling, Y.; Mao, Z.; Wei, J. *ACS Nano* **2014**, *8* (10), 10396. doi: 10.1021/nn505253p
- (30) Kim, Y. J.; Park, W.; Yang, J. H.; Kim, Y.; Lee, B. H. *IEEE J. Electron Dev.* **2018**, *6*, 164. doi: 10.1109/JEDS.2017.2781250
- (31) Calizo, I.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N. *Nano Lett.* **2007**, *7* (9), 2645. doi: 10.1021/nl071033g
- (32) Kaasbjerg, K.; Thygesen, K. S.; Jacobsen, K. W. *Phys. Rev. B* **2012**, *85* (11), 115317. doi: 10.1103/PhysRevB.85.115317
- (33) Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. *ACS Nano* **2010**, *4* (5), 2695. doi: 10.1021/nn1003937
- (34) Thirupuranthaka, M.; Late, D. J. *ACS Appl. Mater. Inter.* **2014**, *6* (2), 1158. doi: 10.1021/am404847d

-
- (35) Thripuranthaka, M.; Kashid, R. V.; Rout, C. S.; Late, D. J. *Appl. Phys. Lett.* **2014**, *104* (8), 081911. doi: 10.1063/1.4866782
- (36) Gutiérrez, H. R.; Perea-López, N.; Elías, A. L.; Berkdemir, A.; Wang, B.; Lv, R.; López-Urías, F.; Crespi, V. H.; Terrones, H.; Terrones, M. *Nano Lett.* **2013**, *13* (8), 3447. doi: 10.1021/nl3026357
- (37) Berkdemir, A.; Gutiérrez, H. R.; Botello-Méndez, A. R.; Perea-López, N.; Elías, A. L.; Chia, C. I.; Wang, B.; Crespi, V. H.; López-Urías, F.; Charlier, J. C.; *et al. Sci. Rep.* **2013**, *3*, 1755. doi: 10.1038/srep01755
- (38) Peimyoo, N.; Shang, J.; Yang, W.; Wang, Y.; Cong, C.; Yu, T. *Nano Res.* **2015**, *8* (4), 1210. doi: 10.1007/s12274-014-0602-0
- (39) Lanzillo, N. A.; Birdwell, A. G.; Amani, M.; Crowne, F. J.; Shah, P. B.; Najmaei, S.; Liu, Z.; Ajayan, P. M.; Lou, J.; Dubey, M.; *et al. Appl. Phys. Lett.* **2013**, *103* (9), 093102. doi: 10.1063/1.4819337
- (40) Sahoo, S.; Gaur, A. P. S.; Ahmadi, M.; Guinel, M. J. F.; Katiyar, R. *S. J. Phys. Chem. C* **2013**, *117* (17), 9042. doi: 10.1021/jp402509w
- (41) Najmaei, S.; Ajayan, P. M.; Lou, J. *Nanoscale* **2013**, *5* (20), 9758. doi: 10.1039/C3NR02567E
- (42) Feng, X.; Kulish, V. V.; Wu, P.; Liu, X.; Ang, K. W. *Nano Res.* **2016**, *9* (9), 2687. doi: 10.1007/s12274-016-1156-0