A unified approach and descriptor for the thermal expansion of two-dimensional transition metal dichalcogenide monolayers

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Two-dimensional (2D) materials have enabled promising applications in modern miniaturized devices. However, device operation may lead to substantial temperature rise and thermal stress, resulting in device failure. To address such thermal challenges, the thermal expansion coefficient (TEC) needs to be well understood. Here, we characterize the in-plane TECs of transition metal dichalcogenide (TMD) monolayers and demonstrate superior accuracy using a three-substrate approach. Our measurements confirm the physical range of 2D monolayer TECs and, hence, address the more than two orders of magnitude discrepancy in literature. Moreover, we identify the thermochemical electronegativity difference of compositional elements as a descriptor, enabling the fast estimation of TECs for various TMD monolayers. Our work presents a unified approach and descriptor for the thermal expansion of TMD monolayers, which can serve as a guideline toward the rational design of reliable 2D devices.

INTRODUCTION

Subnanometer thin two-dimensional (2D) materials and their heterogeneous integration have shown promise to meet the demands for the miniaturization of modern electronic and photonic devices (1, 2). Strong interest in such atomically thin systems has been intensified owing to the recent discovery of direct bandgap (3), high carrier mobility (4), and strong spin–orbit coupling strength (5) in transition metal dichalcogenides (TMDs), which have enabled new frontiers for field-effect transistors (6), light-emitting diodes (7), and spintronics (8). To enable practical application of 2D devices, the thermal expansion coefficient (TEC, α) is one of the most important thermophysical properties of materials to be understood. On the one hand, the van der Waals (vdW) integration of 2D materials on dissimilar materials with TEC mismatch causes failure in epitaxial growth and material transfer, where the accurate characterization of TECs is critical (9, 10). On the other hand, thermal management for miniaturized devices has become increasingly challenging because of the highly localized heat generation (11, 12). The presence of ultrahigh thermal isolation across vdw interfaces limits heat dissipation (13, 14) and can lead to substantial temperature rise (>150°C) (12, 15), which induces large thermal stresses that degrade device performance and accelerate device failure (15–17). Therefore, it is of critical importance to better understand the thermal expansion of 2D materials to optimize materials growth and transfer processes and improve the performance, reliability, and longevity of devices by minimizing thermal mismatch.

Nevertheless, the lack of in-depth understanding and inconsistent measurements of TECs have limited the ability for 2D materials to be used in practical applications. The TECs of 2D materials are difficult to directly measure since 2D materials are atomically thin and optically transparent. Previous works have used various metrologies to characterize TECs of 2D materials, such as scanning electron microscopy (18), transmission electron microscopy (19), X-ray diffraction (20), atomic force microscopy (21), and Raman spectroscopy (16, 22–26). Despite tremendous efforts, only the TECs of a small portion of 2D materials have been studied in the past decade, and there exists a large discrepancy by more than two orders of magnitude for the same 2D material among the existing experimental characterizations (24, 26–28), from ~10⁻⁴ K⁻¹ (thermally expanding like liquids or polymers) to ~10⁻⁷ K⁻¹ (as rigid as fused silica). The key challenge is that the substrate introduces strong effects of out-of-plane coupling (29, 30) and nonuniform in-plane strain, while these experimental approaches typically neglect appropriate interpretation of such effects into measurements (22, 24–26). Therefore, the understanding of TECs of 2D materials had heavily relied on theoretical modeling, such as molecular dynamics (MD) simulations (31, 32) and first-principles calculations (33–35), yet without rigorous experimental support. However, first-principles calculations typically predict Grüneisen parameters that require detailed phonon-level calculations, which makes it difficult to directly translate these atomistic insights to guide practical material selection (34, 35). It is thus an unresolved question what the physical range of TECs of 2D materials is and what dominant physics dictates their differences, making it challenging to understand 2D thermal expansion and optimize materials development and device design.

To address the above challenges, accurate experimental characterization that can decouple the substrate effect and extract the TEC of freestanding 2D materials is needed. Raman spectroscopy has been instrumental in characterizing thermal transport of miniaturized devices by capturing the response of phonons to temperature change, stress, and electric field (30, 36–41). Recent studies have implemented Raman spectroscopy to characterize the TECs of graphene (22, 25), hexagonal boron nitride (40), and MoS₂ (24, 26). However, conventional approaches with Raman spectroscopy rely on either empirical parameters or fitting enabled by theoretical calculations and fail to fully decouple the substrate effect (22, 24–26, 40). Therefore,
these approaches provide highly inconsistent results, and the TECs of 2D materials remain largely unknown (22, 24–26). Recently, we demonstrated a three-substrate approach that can accurately measure the TEC of MoS$_2$ (16). The three-substrate approach combines independent Raman measurements on the three different substrates and decouples the contributions of temperature and substrate effects to the change of Raman peak positions. In this work, we show that we can accurately extract in-plane TECs of several TMD monolayers, MX$_2$ (M = Mo, W; X = S, Se), using the three-substrate approach and address the large discrepancy reported in the literature by confirming the physical range of 2D TMD TECs. Our experimental characterization of the TECs of several TMD monolayers shows excellent agreement with the atomistic modeling. With insights gained from experiments, we confirm a much narrower physical range of in-plane TECs of TMD monolayers, from $5 \times 10^{-6}$ to $\times 10^{-5}$ K$^{-1}$, as compared to the previously reported range, from $\times 10^{-7}$ to $\times 10^{-4}$ K$^{-1}$ (24, 26, 27). Owing to the superior accuracy of our experimental characterization, the dependence of TECs on different compositional elements of TMDs within this narrow physical range can be well resolved. In particular, we show that the TEC of 2D TMDs linearly decreases with the dimensionless thermochemical electronegativity difference of compositional elements. This indicates that the thermochemical electronegativity difference can be used as a fundamental descriptor to elucidate the variations among TECs of TMDs and provide a new path to better understand 2D thermal expansion. To further guide material selections for the practical device design, we provide an empirical correlation between the TEC and the thermochemical electronegativity difference, which enables the rapid estimation of unknown TECs for various TMDs. Our work presents a unified approach and descriptor to characterize and understand the thermal expansion of monolayer TMDs, which can broadly affect fundamental understanding, materials growth, transfer, and device thermal management of 2D TMDs.

RESULTS
The coupled temperature and substrate effect
We elucidate the impact of temperature and substrate on a 2D film in Fig. 1A. As an example, we consider a 2D film supported by a bulk substrate with a smaller TEC. This 2D film is initially in thermal equilibrium with the substrate at room temperature. At the elevated temperature, both the 2D film and the substrate thermally expand. However, compared with the thermal expansion of a freestanding 2D film (① in Fig. 1A), the thermal expansion of the substrate-supported 2D film (② in Fig. 1A) is constrained because of thermal mismatch between the 2D film and the substrate. As a result, there is compressive thermal stress ($\sigma_s < 0$) within the 2D film, which can be described by the strain-stress relations

$$\varepsilon_s = \alpha T + \frac{1 - v}{E} \sigma_s = \alpha_s \Delta T$$

where $\varepsilon_s$ is the in-plane thermal strain within the 2D film when being supported by the substrate, $\alpha$ is the TEC of the 2D film, $\Delta T$ is the temperature rise, $v$ and $E$ are the Poisson’s ratio and the Young’s modulus of the 2D film, $\sigma_s$ is the in-plane thermal stress within the 2D film due to thermal mismatch, and $\alpha_s$ is the linear TEC of the substrate material. The relation holds valid when the thickness of the substrate (\textless mm) is much larger than that of the 2D film (\textless nm). For a highly thermal-expanding substrate, the 2D film will instead have tensile stress ($\sigma_s > 0$) with a temperature rise. The coupled temperature and substrate effect can be captured by Raman spectroscopy through (16, 42)

$$\Delta \omega_s = A_s^{(n)} \Delta T + K_s^{(n)} \sigma_s$$

where $\Delta \omega_s$ is the change of Raman peak position, $n$ represents the Raman-active vibrational mode, $A_s^{(n)}$ is the freestanding temperature coefficient, and $K_s^{(n)}$ is the stress coefficient. Since $\epsilon_s$ is induced by $\Delta T$ (Eq. 1), the coupled effect on $\Delta \omega_s$ can also be represented as (Eq. 2). For a free-standing 2D film, there is no thermal stress upon a temperature rise, so $\Delta \omega_s = A_s^{(n)} \Delta T$.

Figure 1B illustrates the coupled effect of temperature and substrate with the schematic Raman spectra of the 2D film (Eq. 2). The Raman spectra of the 2D film on a low $\alpha$ substrate, freestanding 2D film, and 2D film on a high $\alpha$ substrate at room temperature are plotted in gray, blue, and orange shaded areas, respectively (Fig. 1B). The corresponding Raman spectra at the same elevated temperature are colored red, which shows a red shift due to phonon softening (indicated by the arrows). The length of arrows represents the change of Raman peak positions of the 2D film, which is determined by the substrate-dependent temperature coefficients $A_s^{(n)}$ according to Eq. 3. The freestanding 2D film can be prepared by suspending the sample on microfabricated holes or slots. It can be clearly seen that $|\Delta \omega_{s2}| > |\Delta \omega_{s0}| > |\Delta \omega_{s1}|$ and $|A_{s2}| > |A| > |A_{s1}|$ because compared to the freestanding 2D film, the low $\alpha$ substrate and the high $\alpha$ substrate give compressive and tensile thermal stresses, which turn out to reduce and amplify the temperature dependence of Raman peak position change, respectively (Eq. 3). In this work, we used monolayer TMD as a representative material. Figure 1C shows the top view and the side view of the lattice structure of the TMD monolayer. Figure 1D shows the freestanding 2D film and the in-plane shear mode $E'$ can be detected by Raman spectroscopy (16, 45).

Extracting in-plane 2D TECs using the three-substrate approach
The above coupled temperature and substrate effect is one of the key bottlenecks to realize accurate measurement of TECs of 2D materials via conventional Raman spectroscopy-based approaches. However, the three-substrate approach can extract TECs by taking advantage of the strong temperature- and substrate-dependent Raman signatures (16). Figure 2A shows the concept of the three-substrate approach using micro-Raman spectroscopy with a laser spot diameter of \textless 1 $\mu$m. The single-crystalline monolayer TMD flakes were transferred via a wet transfer process onto three different substrates: a fused silica substrate (SiO$_2$, shown in Fig. 2B), a thermal oxide on silicon substrate with a micro-hole array (Fig. 2C), and a high-purity copper substrate (Fig. 2D), respectively. A thermal stage was interfaced with the bottom of the substrates to control the temperature for Raman measurements (see Materials and Methods.
for more information about sample preparation and Raman measurements. On the holey substrates, 2D monolayers were suspended over the hole area (Fig. 2B), where the diameter of the hole and the distance between adjacent holes are 5 \( \mu \) m. Because of the large aspect ratio of the hole diameter to the thickness of the 2D monolayer (\( \approx 5000 \)), the compressive stress can be relaxed via buckling such that the 2D monolayers can be viewed as freestanding and can freely expand subject to the temperature increase (16, 42, 46).

Figure 2 (B to D) shows \( \times 100 \) magnification optical images of single-crystalline monolayer TMD flakes transferred on the fused silica substrate, the holey substrate, and the copper substrate, after being synthesized by chemical vapor deposition (CVD). The freestanding 2D monolayer flake, highlighted with the dashed triangles, was large enough (\( \approx 25 \mu m \)) to cover the hole area (\( \approx 5 \mu m \) diameter), marked with a dashed circle. MoSe\(_2\) was chosen as an example, and the optical images of other TMD monolayers characterized in
In this work, including monolayer WS₂ and WSe₂, can be found in section S1, where their monolayer nature was also confirmed by photoluminescence spectra (47–50). Temperature-dependent Raman measurements were performed on freestanding monolayer flakes to extract temperature coefficient $A^{(n)}$ and substrate-supported monolayer flakes to extract temperature coefficients $A^{(n)}_{\text{SiO}_2}$ and $A^{(n)}_{\text{Cu}}$ for each 2D TMD (see Materials and Methods for the details of Raman measurements). With temperature coefficients characterized on the three substrates, the in-plane TECs of TMD monolayers are determined by (see Materials and Methods for the derivation of the three-substrate approach)

$$\alpha = \frac{(A^{(n)}_{\text{SiO}_2} - A^{(n)}_{\text{Cu}}) \alpha_{\text{SiO}_2} - (A^{(n)}_{\text{SiO}_2} - A^{(n)}_{\text{SiO}_2}) \alpha_{\text{Cu}}}{A^{(n)}_{\text{SiO}_2} - A^{(n)}_{\text{SiO}_2}}, n = A_1^I or E' \quad (4)$$

where $\alpha_{\text{SiO}_2} = 0.55 \times 10^{-6} \text{K}^{-1}$ and $\alpha_{\text{Cu}} = 16.5 \times 10^{-6} \text{K}^{-1}$. As the theoretical framework is based on symmetry and perturbation analysis, the three-substrate approach is generally applicable to thin films and 2D materials, including those belonging to other symmetry groups (16).

Figure 3 (A and B) shows Raman spectra with temperatures increasing from 20° to 200°C with an interval of 20°C for the fused silica-supported and the freestanding WS₂. The copper-supported WS₂ was only heated up to 160°C for Raman measurements to avoid copper oxidation, as shown in Fig. 3C. Raman red shifts of the in-plane $E'$ mode were observed with increased temperature, as indicated by the dashed lines. Raman spectra of MoSe₂ and WSe₂ can be found in section S2. The residual stress from sample preparation may lead to variations of the initial Raman peak positions on different substrates. However, these variations only alter the absolute positions of Raman peaks and do not affect the temperature coefficients (16). Figure 3D depicts the change of Raman peak positions relative to their initial peak positions at 20°C as a function of temperature for the $E'$ mode of WS₂ on the three substrates. The uncertainty of each Raman measurement was estimated as the standard deviation (SD) of three independent Raman measurements. The change of Raman peak positions with temperature rise has shown strong substrate dependence and good linear trends. The temperature coefficients were extracted from the slopes by linearly fitting (dashed lines of Fig. 3D) with $R^2 > 0.99$. The $R^2$ values of the linear fitting for all the temperature coefficients can be found in table S1. The linear relation between the change of Raman peak positions and temperature rise also indicates that there was no slip between the 2D monolayers and the substrates in the temperature range of our measurements due to the sufficiently strong vdW interactions (16, 46). Specifically, the temperature coefficient of the freestanding WS₂ monolayers $A^{16}_E$ was $-0.0142 \pm 0.0003 \text{cm}^{-1} \text{K}^{-1}$, where the uncertainty of temperature coefficient was estimated as the 95% confidence interval of linear regression. In comparison, the temperature coefficient of the WS₂ monolayer transferred to the fused silica substrate $A^{16}_E = -0.0105 \pm 0.0002 \text{cm}^{-1} \text{K}^{-1}$, whose magnitude was smaller than $|A^{16}_E|$, indicating that the thermal mismatch between WS₂ monolayers and the fused silica substrate induced compressive stress. However, the temperature coefficient of WS₂ monolayer on the copper substrate $A^{16}_E = -0.0211 \pm 0.0006 \text{cm}^{-1} \text{K}^{-1}$, whose magnitude was larger than $|A^{16}_E|$ because of the tensile stress from the highly thermal-expanding copper substrate. Figure 3 (E and F) shows the temperature coefficient characterizations for the $A_1^I$ modes of monolayer MoSe₂ and WSe₂. Note that the $A_1^I$ mode and the $E'$ mode of monolayer WSe₂ are almost degenerate at approximately 250 cm$^{-1}$ (see the Raman spectra of WSe₂ in section S2), and both were used in literature (51). We denote the detected mode of WSe₂ as $A_1^I$ mode to be consistent with that of MoSe₂. The temperature coefficients of MoSe₂ and WSe₂ followed the same trend $|A^{(n)}_{\text{Cu}}| > |A^{(n)}_{\text{SiO}_2}| > |A^{(n)}_{\text{SiO}_2}|$. The results of the temperature coefficient characterization are summarized in Table 1.

Incorporating the measured temperature coefficients into Eq. 4, the in-plane TEC of monolayer WS₂ was $(6.1 \pm 0.6) \times 10^{-6} \text{K}^{-1}$ for the $E'$ mode. In addition to the $E'$ mode, the $A_1^I$ mode of WS₂ at approximately 416 cm$^{-1}$ was also detectable (Fig. 3, A to C). For this reason, we also extracted the TEC of WS₂ monolayer from the $A_1^I$ mode independently. The TEC characterized using the $A_1^I$ mode of WS₂ is $(5.3 \pm 1.7) \times 10^{-6} \text{K}^{-1}$, which showed good consistency with the TEC of the $E'$ mode (see section S3 for the details). This result indicated that the three-substrate approach is a highly self-consistent approach to measure the TECs of 2D materials. The detailed uncertainty analysis of the three-substrate approach can be found in section S4. Since the three-substrate method relied on the calibration in the temperature range from 20° to 200°C, the good linear relationship between the change of Raman peak position and the temperature rise indicated that the TEC remained approximately constant within this temperature range. Considering that this temperature range is the typical operating range of 2D devices, our characterized TEC values are useful to guide practical design. We also performed MD simulation to confirm the insignificant temperature dependence of TECs of TMD monolayers from 20° to 200°C (see Materials and Methods and section S5 for more information). Only MS₂ (M = Mo, W) monolayers were studied here as the force field used cannot well describe the mechanical properties of MSe₂ (M = Mo, W) monolayers (52–54). The negligible temperature dependence of TECs from 20° to 200°C was also confirmed by density functional theory (DFT) calculations (35). The TECs determined from MD showed good agreement with our experiments. The TECs of TMDs characterized in this work are summarized in Table 1. We report the TEC of WS₂ as $(6.1 \pm 0.6) \times 10^{-6} \text{K}^{-1}$ with low experimental uncertainty because it was characterized from the shear mode $E'$, which is more sensitive to in-plane thermal stress.

The physical range and descriptor for 2D TMD TEC

To further confirm experimental accuracy, we compared the TECs obtained from the three-substrate approach with DFT calculations (35) in Fig. 4A and observed excellent agreement. Both experimental and theoretical results show that the TECs of TMD monolayers are on the order of $10^{-6} \text{K}^{-1}$. Our accurate measurements addressed the large discrepancies of 2D TMD TECs found in literature. Specifically, Hu et al. (27) performed a first-principles modeling–assisted experimental approach and showed that the in-plane TECs of TMD monolayers were $\sim 10^{-4} \text{K}^{-1}$, which is comparable with the TECs of polymers and liquids and two orders of magnitude higher than typical semiconductors ($\sim 10^{-6} \text{K}^{-1}$) (55). Lin et al. (24) also studied 2D MoS₂ using Raman spectroscopy without experimentally incorporating the substrate effect and reported the TEC to be approximately $5 \times 10^{-7} \text{K}^{-1}$ at room temperature, which is comparable with the TECs of the most rigid materials like fused silica (55) and more than two orders of magnitude lower than the TEC given by Hu et al. (27). In addition, Anemone et al. (28) claimed that the natural bulk MoS₂ lattice parameter was found to remain constant in a large temperature range, where they concluded that the TEC of MoS₂ is zero. To elucidate the discrepancies of 2D TMD TECs due to inaccurate measurements, we tabulated TECs of various materials.
in Table S3, showing a physical spectrum of thermal expansion regimes from liquids to solids. Since the mechanism of thermal expansion is governed by interatomic bond strength and thermal effects, the TECs of 2D materials with the same lattice structures should be within the similar range on the order of $10^{-6}$ K$^{-1}$ above the Debye temperature. Therefore, through our accurate experimental measurements, we confirm that the TECs of 2D TMDs (from $5 \times 10^{-6}$ to $1 \times 10^{-5}$ K$^{-1}$) fall into the same physical range as the TECs of common semiconductors (~$10^{-6}$ K$^{-1}$) (55). In general, the TECs of TMD monolayers are higher than the bulk values reported in the literature (27, 56–58), which is attributed to the absence of interlayer vdW interactions (16). However, further experimental and theoretical efforts need to be pursued to not only provide accurate measurements of bulk TECs but also better understand the physical origin of the difference between 2D and bulk thermal expansion.

Owing to the highly accurate characterization, we can further understand the role of compositional elements in determining TECs of 2D TMDs. Within the physical range, our experiments show consistent compositional element dependence of TECs with DFT calculations (Fig. 4A). For example, the TEC of MoX$_2$ is larger than that of WX$_2$ (X = S, Se, Te), while the TEC of MS$_2$ is smaller than that of MSe$_2$ (M = Mo, W). With quasi-harmonic approximations, theoretical studies typically predict the TEC by calculating Grüneisen parameters for individual phonon modes from a thermodynamic
point of view (22, 35). Although these first-principles approaches can provide detailed information of various fundamental parameters, it is still difficult to construct a simple and clear physical picture to interpret these interesting trends and further guide materials development and selection. As the thermal expansion is the interplay of chemical bonding and thermal effects, the thermochemical nature of M–X bonds is crucial. Compared with the Grüneisen parameters, which require expensive computation, the electronegativity difference between the metal and chalcogen atoms is not only much more widely accessible but also a simpler fundamental parameter describing the polar nature of M–X bonds (59, 60). Specifically, the concept of electronegativity was developed by Pauling in 1931 (59), describing the tendency of an atom of a given element to attract shared electrons in a covalent bond with a unit of eV/1/2. A higher value of the electronegativity indicates that the element attracts the shared electrons more strongly. Tantardini and Oganov (60) further reformulated Pauling’s electronegativity with experimental dissociation energies, which leads to the dimensionless thermochemical electronegativity. Figure 4B shows that Tantardini and Oganov’s dimensionless thermochemical electronegativity difference $\Delta \chi_{M-X}$ between M and X atoms can well capture the variations in the TECs of monolayer TMDs, where a decreasing linear dependence between $\Delta \chi_{M-X}$ and TECs was observed. This trend is because a larger $\Delta \chi_{M-X}$ indicates a stronger polarity between M and X atoms. As a result, the material is stiffer, and its thermal expansion becomes lower (35, 61, 62). The validity of using $\Delta \chi_{M-X}$ to qualitatively describe the properties of M–X bonds was also confirmed in a study focused on the mechanical properties of atomically thin WX$_2$ (54). We further show the strong dependence among the in-plane stiffness predicted using DFT calculations (35), electronegativity difference, and TECs of 2D TMD in section S7. The close relationship indicates that thermochemical electronegativity difference is a fundamental, intuitive, and simple descriptor to the TECs of TMD monolayers. Furthermore, since the value of the thermochemical electronegativity for each element is already available (60), the discovery of the linear dependence between $\alpha$ and $\Delta \chi_{M-X}$ can enable a rapid estimation of unknown TECs of other 2D TMD in practical applications without complex first-principles computations and experiments. Therefore, we suggest the following empirical correlation to estimate $\alpha$ using $\Delta \chi_{M-X}$ as a descriptor, by fitting our experimental data and existing theoretical predictions with a line (dashed line in Fig. 4B)

$$\alpha = k \Delta \chi_{M-X} + \beta$$  (5)

where $k = -6.1 \times 10^{-6}$ K$^{-1}$ and $\beta = 13.1 \times 10^{-6}$ K$^{-1}$. The $R^2$ of the linear fitting is 0.6192, and the uncertainties of $k$ and $\beta$, estimated as the 95% confidence intervals, were $1.7 \times 10^{-6}$ and $1.5 \times 10^{-6}$ K$^{-1}$, respectively. The estimation uncertainty of the empirical correlation $\alpha = 1.71 \times 10^{-6}$ K$^{-1}$ was evaluated as 1 SD of linear fitting (the gray uncertainty band in Fig. 4B).

DISCUSSION

We performed a three-substrate approach to extract the in-plane TECs of 2D TMD monolayers based on micro-Raman spectroscopy. The purely experimental approach considered thermal mismatch and free expansion and was carried out by temperature-dependent Raman measurements on three substrates, including a holey substrate, a fused silica substrate, and a copper substrate, to decouple substrate and temperature effects. Our measurements show excellent agreement with atomistic simulation, which addresses the large discrepancy in the literature and confirms the physical range of in-plane TECs of 2D TMD monolayers (from $5 \times 10^{-6}$ to $1 \times 10^{-5}$ K$^{-1}$) that was not well understood before. Owing to the high accuracy, this unified approach can even resolve the impact of elements on the TECs of TMD monolayers. We showed that the dimensionless thermochemical electronegativity difference can elucidate the variations among TECs of several TMDs monolayers and suggested an empirical correlation to rapidly estimate the TECs of various TMDs. Our work presents a unified approach and descriptor to characterize and understand the thermal expansion of 2D TMD monolayers, which can serve as a reference to optimize material growth and transfer processes, and improve the...
performance, reliability, and longevity of devices by minimizing thermal mismatch.

**MATERIALS AND METHODS**

**Material growth**

Monolayer WSe$_2$ flakes were grown under low pressure by metalorganic CVD. Tungsten hexacarbonyl [W(CO)$_6$, Sigma-Aldrich] and dimethyl selenide [(CH$_3$)$_2$Se, Sigma-Aldrich] were selected as precursors of W and Se, respectively, and were supplied in a gas phase into a 2.45-cm quartz tube furnace by the help of a bubbler system with Ar as a carrier gas. The WSe$_2$ flakes were synthesized on a 300-nm-thick SiO$_2$/Si wafer with the flow rate of 100 standard cubic centimeters per minute (scm) of Ar, 1 scm of H$_2$, 0.3 scm of W(CO)$_6$, and 0.05 scm of (CH$_3$)$_2$Se for 5 hours under the growth temperature of 420°C. After growth, the furnace heat was turned down, and the furnace was cooled down until it reached room temperature. The WSe$_2$ samples used in this work were purchased from the fused silica and copper substrates, respectively. The Raman peak positions were obtained by fitting experimental data to the Voigt profile (16, 38). The uncertainty of each Raman peak position was estimated from the SD of three independent measurements.

**Description of the three-substrate approach**

The strain-stress relations of the 2D film supported by the fused silica and copper substrates can be expressed as

$$\varepsilon_{\text{SiO}_2} = \alpha \Delta T + \frac{1-v}{E} \sigma_{\text{SiO}_2} = \alpha_{\text{SiO}_2} \Delta T$$

(6)

$$\varepsilon_{\text{Cu}} = \alpha \Delta T + \frac{1-v}{E} \sigma_{\text{Cu}} = \alpha_{\text{Cu}} \Delta T$$

(7)

where $\varepsilon_{\text{SiO}_2}$ and $\varepsilon_{\text{Cu}}$ are the in-plane strains of the 2D films supported by the fused silica and copper substrates, respectively. $\sigma_{\text{SiO}_2}$ and $\sigma_{\text{Cu}}$ are the corresponding in-plane thermal stresses in the 2D films induced by the substrates. Plugging Eqs. 6 and 7 into Eq. 2, the coupled temperature and substrate effect on the change of Raman peak positions through thermal stresses $\sigma_{\text{SiO}_2}$ and $\sigma_{\text{Cu}}$ can be explicitly written in the form of Eq. 3

$$\Delta \omega^{(n)}_{\text{SiO}_2} = \left( \frac{K^{(n)}(\alpha_{\text{SiO}_2} - \alpha') E}{1-v'} \right) \Delta T = A^{(n)}_{\text{SiO}_2} \Delta T, n = A_i or E'$$

(8)

$$\Delta \omega^{(n)}_{\text{Cu}} = \left( \frac{K^{(n)}(\alpha_{\text{Cu}} - \alpha') E}{1-v'} \right) \Delta T = A^{(n)}_{\text{Cu}} \Delta T, n = A_i or E'$$

(9)

Equations 8 and 9 indicate that the stress coefficient $K^{(n)}$ and the constant term $\frac{E'}{1-v'}$ can be eliminated, and the TEC $\alpha$ can be related to temperature coefficients of the Raman measurements $A^{(n)}_{\text{SiO}_2}$, $A^{(n)}_{\text{Cu}}$, and $A^{(n)}$ using Eq. 4.

**MD simulation**

Classical MD simulation was performed to calculate the TEC using the LAMMPS package (63). The freestanding TMD monolayer was approximately 50 nm long along each in-plane direction. The intermolecular interactions were modeled by Stillinger-Weber potentials (64). Periodic boundary conditions were applied to the in-plane directions, while no restriction was applied to the cross-plane direction. With a timestep of 0.5 fs, the monolayer was initially relaxed in a constant pressure (zero) condition for 3 ns, followed by 2 ns used to record the free expanding length. The lattice constants of the material were estimated at different temperatures so that it can be expressed as a function of temperature. The linear TEC $\alpha_i(T)$ can be calculated using

$$\alpha_i = \frac{1}{l} \frac{\partial l}{\partial T}$$

(10)

where $l$ is the lattice constant of the TMD monolayer, and $i$ indicates the in-plane direction of the simulation domain. The reported TEC using MD simulation is the average TEC $\bar{\alpha}$ since no strong anisotropy was observed along the two in-plane directions. More details can be found in section S5.

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