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High Temperature Behavior of Monolayer WS₂ and Its Interaction with Substrate: Dependence on Substrate Type and Bonding

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Abstract
This study reveals that interaction between a 2D material and its substrate can drastically modify its electronic and optical properties, and thus is of fundamental interest and can be used as a versatile means to tune the properties. High temperature (25 – 500 °C) optical spectroscopy, which combines Raman and photoluminescence spectroscopies, is shown to be highly effective for probing the interaction and studying material properties that are not accessible at the commonly used cryogenic temperature (e.g., a thermal activation process with an activation of a major fraction of the bandgap). We investigate a set of monolayer WS₂ films, either directly grown on sapphire and SiO₂ substrates by CVD or transferred onto SiO₂ substrate. The coupling with the substrate is shown to depend on not only substrate type but also the material-substrate bonding even for the same substrate as well as the excitation wavelength. The inherent difference in the states of strain between the as-grown and transferred films has a major impact on the material properties.

Keywords: Tungsten disulfide, high temperature, Raman, temperature coefficient, photoluminescence, activation energy

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1 Introduction

Following the discovery of two-dimensional (2D) materials such as graphene and boron nitride [1-4], graphene analogues of other layered materials with similar hexagonal structure, especially those compounds involving transition metal dichalcogenides (TMDs) [5], have recently attracted significant attention due to their various physical, chemical and mechanical properties that could be promising candidates for various applications [6-13]. The basic building block of TMDs consists of one atomic layer of transition metal atoms sandwiched by two chalcogen atomic layers, together referred to as one monolayer (1L), as shown in Figure 1(a). Bulk TMD crystals are typically semiconductors with an indirect band gap in the near infrared spectral range, while monolayer TMDs such as molybdenum disulfide (MoS$_2$), tungsten disulfide (WS$_2$), or tungsten diselenide (WSe$_2$) have a direct band gap in the visible spectral range, in contrast to graphene’s zero gap and monolayer hexagonal boron nitride’s (h-BN) large gap of > 5 eV [13-16]. Besides the property of indirect-to-direct bandgap transition with reducing the layer number, the monolayer or 2D transition metal disulfides 2D-MS$_2$ (M = W, Mo), which have been intensively studied among the 2D-TMDs, exhibit a high carrier mobility of approximately 200 cm$^2$·V$^{-1}$·s$^{-1}$, strong spin-orbit coupling, and weak room temperature (RT) ferromagnetism [17-21]. Therefore, 2D-MS$_2$ has broad potential for next-generation electronic and optical device applications, such as flexible heterostructures of graphene-WS$_2$ for field effect tunneling transistors [22, 23].

However, with very few exceptions, the reported properties of TMDs were obtained with the film supported by a substrate. The well-known effects of the substrate may include charge doping, which often results in changes in the peak position and intensity of a spectral feature (e.g., in Raman and photoluminescence spectroscopies) [24, 25], and a change in dielectric environment, which affects the optical contrast of the film against the substrate and further leads to an optical
interference effect that can affect the signal strength of the spectroscopy feature [26]. These studies were typically done with mechanically exfoliated and transferred films. We have recently discovered a more subtle substrate effect with MoS\textsubscript{2} [27], namely, the film-substrate interaction depends on the mesoscopic film morphology that in turn depends on whether the film is directly grown on or mechanically transferred onto the substrate, and the difference in film morphology leads to drastically different temperature shifts for the in-plane and out-of-plane lattice vibration modes. This finding suggests that the surface morphology difference could significantly impact the in-plane electronic transport through electron-phonon coupling that is sensitive to the symmetry of the vibration mode [28]. We point out that in contrast to cooling the sample to cryogenic temperature, heating the film to material decomposition temperature can provide either complementary or more valuable insight to the film-substrate interaction for these considerations: (1) at an elevated temperature the film is more likely to re-arrange its bonding with the substrate, which is relevant to the annealing effect; (2) the possibility to evaluate the effect of the built-in strain associated with the thermal expansion coefficient (TEC) mismatch between the film and substrate after cooling from the growth temperature; (3) the ability to probe thermal activation processes that exhibit larger activation energies than room temperature can offer; (4) the actual operating temperature of a thin-film device is often substantially higher than the intended room temperature. Most of these points are in fact more relevant for the 2D materials than traditional 3D materials, because the nature of the film-substrate bonding is very different, and as a consequence, heat dissipation in the 2D material is very different and challenging, for instance, self-heating in the WS\textsubscript{2} based device [23]. This type of study may eventually allow us to obtain the intrinsic properties of the idealistic free-standing 2D material from extrapolating the results with substrate.
Raman spectroscopy is a widely used nondestructive technique to characterize the structural and electronic properties of monolayer materials such as graphene and MoS$_2$ [27, 29]. It was recently shown that this technique was suitable for a quick determination of the number of monolayers in WS$_2$, in a similar manner as in MoS$_2$, by the dependence of Raman peak positions on the layer number [30, 31]. Temperature-dependent photoluminescence (PL) spectroscopy is often used to investigate radiative and non-radiative recombination processes and exciton-phonon interactions in semiconductor materials. In general, thermal quenching of the PL intensity with increasing temperature is attributed to the thermal activation of defects or impurities. Such study is usually performed in the temperature range from cryogenic to room temperatures. Higher temperature, in principle, would allow us to probe a defect state with a larger activation energy. However, this technique has rarely been applied above RT, largely because the PL signal is expected to become very weak at higher temperature even for a bulk material that offers a large absorption volume. For this reason, the high temperature measurements are expected to be more challenging for a single monolayer material like WS$_2$.

In this work, we perform temperature-dependent PL and Raman investigations on a set of single monolayer WS$_2$ samples with temperatures up to 500 °C (close to decomposition point). Both Raman and PL measurements indicate the existence of significant coupling between the 2D-WS$_2$ and its substrate, in contrast to the common assumption that the substrate merely provides mechanical support and that the measured properties are mostly intrinsic to the film. Not only do the effects of the substrate vary drastically between the as-grown films on SiO$_2$ and sapphire substrates, but the substrate effects are very different between the as-grown and transferred films on the same substrate type. Beyond the well-known doping effect caused by the chemical residual on the transferred film [32, 33], we show that the inherent difference in the states of strain between
the as-grown and transferred films has a major impact on the material properties. The substrate effect may tune the band structure of WS\textsubscript{2} monolayers, manifesting itself as changes in the optical properties, such as Raman enhancement, PL peak energy, and their temperature dependences. The PL measurements also show a major difference in both RT PL intensity and thermal quenching processes between the samples grown on different substrates. For the 2D-WS\textsubscript{2} on SiO\textsubscript{2}, a thermal quenching process with an activation energy of 0.40 eV is observed, whereas on sapphire, two thermal quenching processes were observed with activation energies of 0.20 eV and 1.51 eV, respectively.

2 Experimental

We have recently demonstrated the growth of large-area single crystalline monolayer WS\textsubscript{2} [34], and a technique to transfer the large film as a whole to a secondary substrate [35]. These developments make the current study possible. Five samples were studied in this work: (a) “1L-SiO\textsubscript{2}” is a monolayer WS\textsubscript{2} film grown on Si substrate coated with 300 nm SiO\textsubscript{2}; (b) “1L-SA-TRI” is triangle shape monolayer WS\textsubscript{2} films grown on sapphire substrate; (c) “1L-SA-FILM” is a large area monolayer WS\textsubscript{2} film grown on sapphire substrate; (d) “1L-TRAN-SiO\textsubscript{2}” is a transferred monolayer WS\textsubscript{2} film originally grown on sapphire; and (e) “bulk-SiO\textsubscript{2}” is a thick layer of WS\textsubscript{2} (>20 monolayers) on the same SiO\textsubscript{2}/Si substrate as “1L-SiO\textsubscript{2}”. Figure 1(b)-(e) shows the optical images of the four samples, with an AFM image of 1L-SA-TRI shown in Figure 1(f). The thickness of the 1L WS\textsubscript{2} was measured to be ~0.7 nm, consistent with the expected thickness of the monolayer [36].

Raman and PL measurements were carried out in a Horiba LabRAM HR800 Micro-Raman system in back-scattering geometry with a spectral resolution better than 1 cm\textsuperscript{-1}. The temperature-
dependent measurements were carried out with a 50× long-working-distance lens (NA = 0.5). A Linkam TS1500 heating system, with temperature control accuracy of 1 °C, was used to heat the samples with a step of 25 °C and heating rate of 10 °C/min. Before acquiring the spectrum, the temperature was held for at least five minutes at each temperature step, allowing sufficient time for stabilization. To prevent the WS₂ films from reacting with oxygen, an extremely low flow rate of nitrogen gas was purged through the sample chamber. A sufficiently low laser power (< 1 mW) was used to minimize sample heating. Two excitation wavelengths were used, 532 nm and 441.6 nm, to examine the excitation wavelength dependence for near and off resonance excitation.

3 Results and Discussion

3.1 Room-temperature Raman and PL and their substrate and wavelength dependences

Figure 2(a)-(e) show typical Raman spectra of all four 1L samples as well as “bulk” WS₂ under both 532 nm and 441.6 nm laser excitation. The corresponding excitation energies are near and off resonant with the B exciton of the material, respectively. A laser power ~150 µW was used. Under 441.6 nm excitation, the four 1L samples exhibit similar spectroscopy features in the spectral region of interest: two optical modes, \(E_{2g}^{1}(\Gamma)\) for the in-plane motion of W + S atoms at ~355 cm\(^{-1}\) and \(A_{1g}(\Gamma)\) for the out-of-plane motion of two S atoms at ~417 cm\(^{-1}\), separated by 61.7 cm\(^{-1}\). The \(E_{2g}^{1}(\Gamma)\) and \(A_{1g}(\Gamma)\) separation has been shown to be a simple signature for the monolayer WS₂.\(^{30}\) For the “bulk” WS₂, the frequency difference between \(E_{2g}^{1}(\Gamma)\) and \(A_{1g}(\Gamma)\) modes is 65 cm\(^{-1}\). The two on-sapphire samples show comparable Raman intensities, whereas the 1L-SiO₂ sample produces a lower signal by a factor of 2–3, but the transferred sample 1LTRAN-SiO₂ has the strongest signal, ~3 times that of the on-sapphire samples.
Under near-resonant excitation of 532 nm, a few additional Raman peaks appear on the lower frequency side of the $E_{2g}^1(\Gamma)$, in particular a very strong second order peak $2LA(M)$ almost overwhelms the $E_{2g}^1(\Gamma)$. A fitting procedure is required to deconvolute the $2LA(M)$ and $E_{2g}^1(\Gamma)$ components. The resonant effect also produces very rich Raman modes in the lower (frequency region and some additional features in the higher frequency region (Figure S1) [31]. The most striking observation from comparing the four 1L samples lies in that the signals of the on-SiO$_2$ samples, both as-grown and transferred, are substantially stronger than those of the other two on-sapphire samples, in particular the 1L-SiO$_2$ is stronger by over a factor of 10-20, and 1L-TRAN-SiO$_2$ by a factor of 3-5. The three as-grown samples display an anti-correlation between the resonant and off-resonant signals, i.e., a stronger resonant signal under 532 nm excitation corresponds to a weaker off-resonant signal under 441.6 nm excitation. The transferred film on SiO$_2$ shows the strongest off-resonant signal, about 10 times of the as-grown sample on the same type of substrate, but about a factor of 3 weaker under near-resonant excitation. These comparisons offer the first indication of substrate and film-substrate bonding dependence of the 2D-WS$_2$ film, and that more than one mechanisms is at work to produce these substrate effects. The relative intensities of different samples at the two excitation wavelengths are summarized in Table 1.

We now analyze the substrate effect on the electronic structure. Monolayer WS$_2$ has two interband transitions near the bulk direct transitions at the K point due to spin-orbit splitting of the valence band, assigned as A (1.95 eV) and B (2.36 eV) excitons [12, 37]. Figure 2(f) shows PL spectra of all the WS$_2$ samples excited with 441.6 nm. In our samples, a weak peak at ~2.35 eV, corresponding to the B exciton, can be seen at room temperature, which indicates the high quality of the CVD-grown 1L WS$_2$. The primary PL band near the fundamental bandgap typically exhibits significant asymmetric broadening on the lower energy side, which can be deconvoluted into two
components using two Gaussian lineshape functions, as shown in Figure S2. The higher energy component is usually attributed to the A exciton of the fundamental bandgap, whereas the lower energy component is interpreted as a negatively charged exciton (A⁻), also known as a trion, resulting from n-type doping due to either charge transfer from the substrate or defects in the film [38, 39]. The variation in the A exciton peak position among these samples is likely due to strain.

For the CVD grown samples, if we assume that the 2D film is deposited on the substrate with very little strain at the growth temperature (typically 900 °C), after cooling to room temperature, the mismatch in TEC between the film and substrate will introduce strain in the film. The TECs of both SiO₂ and sapphire are smaller than WS₂ [40, 41], with SiO₂ being much smaller than WS₂ and sapphire close to, which suggests that more tensile strain is generated in the WS₂ film grown on SiO₂ than on sapphire, leading to the largest redshift of the PL peak energy in the 1L-SiO₂ sample. However, for the transferred sample 1L-TRAN-SiO₂, although on the same type of substrate as 1L-SiO₂, the PL exhibits the highest peak energy, which can be explained as that the strain is released after being transferred. The high lying B-exciton state is more immune to the impurities and defects that are more likely to contribute to the band edge emission. The fact that the B-exciton transition energies follow quite closely those of the band edge emission supports the interpretation that the PL peak shift is due to the strain effect. Based on the PL peak position difference between 1L-SiO₂ and 1L-TRAN-SiO₂ and their theoretically calculated bandgap deformation potential (−0.19 eV/% for tensile strain, using a density functional theory (DFT) [42]), the built-in epitaxial strain in 1L-SiO₂ can be estimated to be 0.47%.

The PL intensity of 1L-TRAN-SiO₂ is much stronger than 1L-SiO₂ by approximately a factor of 5, which is opposite to the relative intensity in Raman where 1L-SiO₂ is much stronger. The small bandgap shift should not significantly affect PL intensity, because of typically weak absorption
strength variation with wavelength. There are two known major effects influencing the intensity of band edge PL emission: (1) doping [24, 25], and (2) optical interference [26]. Stronger bonding for the as-grown sample likely quench the PL relative to the transferred sample with weaker bonding to the otherwise same SiO₂ substrate. However, the PL intensities of the on-SiO₂ samples are in general much stronger than the on-sapphire samples, for instance, by as much as 125 times between 1L-TRAN-SiO₂ and 1L-SA-FILM. The major PL intensity reduction for the on-sapphire samples could be due to non-radiative recombination via substrate. Additionally, the interference effect of the thin-layer SiO₂ could slightly enhance the light absorbed by the WS₂ film and its collection efficiency [26]. Qualitatively similar substrate type dependence was also observed for 532 nm excitation (Figure S2). The relative PL intensities are summarized in Table 1. In short, the SiO₂ substrate offers much stronger PL than sapphire substrate for both excitation wavelengths. These observations illustrate that film-substrate interaction could be rather complex.

Returning to the peculiar wavelength-dependent substrate effect in Raman intensity shown in Figure 2(a)-(e) to compare the two substrate types, in 1L-SiO₂, the 532 nm excitation yields much stronger 2LA(M)/E₂g₁(Γ) Raman signal than 441.6 nm, which is in stark contrast to 1L-SA-TRI and 1L-SA-FILM. In these latter two samples, 441.6 nm excitation instead yields stronger signals than 532 nm excitation. The strong 1L-SiO₂ intensity enhancement under 532 nm excitation can be explained by the resonant Raman effect described below [43]:

$$I(E_L) = K \left| \frac{\langle f | H_{e-r} | b \rangle \langle b | H_{e-ph} | a \rangle \langle a | H_{e-r} | i \rangle}{(E_L - E_g - i\Gamma_a)(E_L - E_{ph} - E_g - i\Gamma_b)} \right|^2$$

where $I(E_L)$ is the Raman scattering intensity, and $K$ is a constant; $|i\rangle$ is the initial state, $|a\rangle$ and $|b\rangle$ are two intermediate states, and $|f\rangle$ is the final state; $H_{e-r}$ and $H_{e-ph}$ are the Hamiltonians of the
radiation of the light and the electron-phonon coupling, respectively; $E_L$ is the energy of the incident light, $E_g$ is the energy of the electronic transition, and $E_{ph}$ is the phonon energy; $\Gamma_a$ and $\Gamma_b$ are the damping constants related to the lifetimes of the two intermediate states $|a\rangle$ and $|b\rangle$, respectively. The 532 nm excitation wavelength (2.33 eV) is very close to the energy of B exciton to yield Resonant Raman scattering. The first term in the denominator of Equation 1 reflects the resonance of the incoming photon with the B exciton transition energy, the second term of the outgoing photon involving the phonon energy. The B-exciton PL emission energy of 1L-SiO$_2$ at 2.31 eV is the closest to the laser energy among the four 1L samples. This sample suggests that the incoming electronic resonant plays a dominant role. Also, the resonant effect was shown to become progressively weaker with reducing the excitation wavelength [31]. Although the Raman intensity difference between the two on-SiO$_2$ samples under 532 nm excitation could be explained by the energy derivation from the resonance condition due to the B exciton energy level difference (2.31 vs. 2.38 eV), the Raman intensity difference under 441.6 nm could be caused by another mechanism that is yet to be determined. One possibility could be the difference in charge transfer or doping.

3.2 High Temperature Raman Scattering

The temperature-dependent Raman study was reported for a 1L mechanically exfoliated (ME) WS$_2$ from 77 to 623 K with the temperature coefficients of both $E_{2g}^1(\Gamma)$ and $A_{1g}(\Gamma)$ modes being $-0.006$ cm$^{-1}$/K, although the data were apparently non-linear in temperature [44]. As shown previously for MoS$_2$, ME film is expected to have very different bonding with the substrate compared to the epitaxial film [27, 45]. Here we perform the high temperature Raman investigations for the four 1L WS$_2$ samples from RT to 500 °C. Figure 3(a) shows the temperature-dependent Raman spectra of 1L-SiO$_2$. For both $E_{2g}^1(\Gamma)$ and $A_{1g}(\Gamma)$ modes, the Raman frequency decreases with increasing
temperature. In addition, the intensity of 2LA(M) decreases drastically as the temperature rises, because the bandgap redshift detunes the laser energy from resonance. Empirically, the temperature dependence of Raman shift can be described as:

$$\omega(T) = \omega_0 + \chi_1 \Delta T + \chi_2 (\Delta T)^2 + \chi_3 (\Delta T)^3,$$  \hspace{1cm} (2)

where $\omega_0$ is the frequency at RT, $\Delta T$ is the temperature change relative to RT, and $\chi_1, \chi_2$ and $\chi_3$ are the first-, second- and third-order temperature coefficients, respectively. For both sapphire samples, note that one of sapphire Raman peaks at 417 cm$^{-1}$ overlaps with WS$_2$ A$_{1g}(\Gamma)$ peak. Thus, sapphire’s spectra were collected at each temperature and carefully subtracted to yield the WS$_2$ Raman spectrum as illustrated in Figure S3.

The change in Raman frequency ($\Delta \omega$) with increasing temperature typically include three contributions [40]:

$$\Delta \omega(\Delta T) = \Delta \omega_E(\Delta T) + \Delta \omega_A(\Delta T) + \Delta \omega_M(\Delta T),$$  \hspace{1cm} (3)

where $\Delta \omega_E$ is due to thermal expansion of the lattice, resulting in a redshift, $\Delta \omega_A$ is attributed to anharmonic effects, i.e. phonon mode softening with increasing vibrational amplitude, and the last term in Equation 3 is related to the TEC mismatch between substrate and WS$_2$ which may introduce a strain, giving rise to a phonon frequency shift. Figure 3(b)-(c) show the temperature dependence of Raman frequency for both E$_{2g}^1(\Gamma)$ and A$_{1g}(\Gamma)$ modes in all the five samples. As a common practice, one might consider both E$_{2g}^1(\Gamma)$ and A$_{1g}(\Gamma)$ as exhibiting linear redshifts with increasing temperature. However, the clearly observable difference in slope among the samples and the subtle non-linearity reflect the intricate film-substrate interactions.
For $E_{2g}^1(\Gamma)$, the previous study on MoS$_2$ indicates that the transferred sample shows the least substrate effect on this in-plane mode [27]. Thus, we may take 1L-TRAN-SiO$_2$ as an approximate reference for a free-standing 1L WS$_2$. In fact, as shown in Figure 3(b), the temperature dependence of this sample is very similar to strain-free bulk MoS$_2$, which shows a weak non-linear effect at high temperature [27]. Other than the small variations in frequency, the temperature shifts of the two on-sapphire samples are very similar to that of the 1L-TRAN-SiO$_2$, indicating relatively small strain in the epitaxial film and weak bonding to the substrate. However, the slopes for the two as-grown samples on SiO$_2$ are substantially smaller than that of 1L-TRAN-SiO$_2$. As suggested by the RT-PL data mentioned above, 1L-SiO$_2$ is under significant tensile strain at RT, and manifests itself as the lowest Raman frequency among all the samples. Thus, the third term in Equation 3 becomes significant. The TEC of WS$_2$ is about one order of magnitude higher than that of SiO$_2$. With increasing temperature, the WS$_2$ film expands faster than SiO$_2$, which in turn results in a relaxation of tensile strain in the WS$_2$ film. The strain relaxation gives rise to a blue shift that compensates the intrinsic red shift given by the first and the second terms in Equation 3, resulting in an apparent smaller temperature coefficient than 1L-TRAN-SiO$_2$ and sapphire samples. This is also largely true for the thicker sample, “bulk”-SiO$_2$, because it is not thick enough to allow the WS$_2$ to fully relax at RT, which explains why its temperature coefficient is higher than that of 1L-SiO$_2$ but lower than the other samples. However, due to the difference of TEC’s between sapphire and WS$_2$ in 1L-SA-TRI and 1L-SA-FILM is relatively small, no significant strain is generated in the films when cooled down to RT. Assuming that the transferred sample is strain free and using a DFT calculated deformation potential of $-5.25 \text{ cm}^{-1}/\%$ under the tensile strain [42], we estimate a tensile strain of 0.67% in 1L-SiO$_2$. The estimated values from both PL and Raman are in very good agreement with that estimated from the TEC difference of 0.69%.
For \( A_{1g}(\Gamma) \), the previous study on MoS\(_2\) indicates that this out-of-plane mode is particularly sensitive to the film’s morphology (e.g., mesoscopic scale mechanical buckling and chemical residues associated with the transferred film), and very strong non-linearity was observed for the transferred film. As shown Figure 3(c), the strongest non-linearity is observed for the transferred film 1L-TRAN-SiO\(_2\), although it is not as drastic as reported for an ME MoS\(_2\) film on SiO\(_2\) [27]. The two as-grown samples on SiO\(_2\) exhibit rather good linearity and with very close slopes. Because the strain-induced \( A_{1g}(\Gamma) \) frequency shift is much smaller (\(-1.94 \text{ cm}^{-1}/\% \text{ under tensile strain from the DFT calculation [42]}\)) than \( E_{2g}^{-1}(\Gamma) \), the relaxation of tensile strain with increasing temperature partially offsets the steeper intrinsic slope initially, which yields a nice linear dependence over the entire temperature range. Therefore, the intrinsic temperature coefficient for a free standing monolayer or bulk WS\(_2\) is expected to be rather close to (but slightly larger than) that of 1L-SiO\(_2\) or “bulk”-SiO\(_2\), respectively. The results for the two on-sapphire samples are perturbed more by the substrate than the on-SiO\(_2\) samples. For the transferred sample, increasing the temperature improves bonding with the substrate (e.g., evaporation of the chemical residues introduced during the film transfer), thus enhancing the charge transfer (n-type doping) from the substrate to the film [24, 25], leading to the phonon frequency red shift [28]. This effect may explain the accelerated redshift in 1L-TRAN-SiO\(_2\) below 100 °C. Upon increasing the temperature further, thermally activated non-radiative recombination tends to deplete the carriers, which results in a less rapid temperature-dependent redshift. Above 250 °C, the temperature dependence approaches that of a free-standing film. This finding suggests that an epitaxial film is expected to have better electronic mobility than the transferred film, because of the symmetry selection rule difference for the electron-phonon coupling between the two modes, specifically, the coupling is
stronger for the $A_{1g}(\Gamma)$ mode [28]. This observation could provide guidance for identifying the optimal thermal annealing process to achieve desirable properties in device applications.

Based on the above discussions for the underlying mechanisms of the phonon frequency change, fitting the experimental data assuming a linear temperature dependence is meaningful by providing an empirical temperature dependence for certain cases. For instance, although more than one mechanisms is at work, in 1L-SiO$_2$ and “bulk”-SiO$_2$, the net effect is more linear and close to that of the intrinsic WS$_2$. For most other cases, linear fitting is not justified. Nevertheless, it can still illustrate significant variations with changing substrate type and bonding. Therefore, we show linear fitting results for all the samples in Table 2, whereas the non-linear fitting results are given in Table S1.

Finally we note that the integrated Raman intensities for both $E_{2g}^\dagger(\Gamma)$ and $A_{1g}(\Gamma)$ modes have been found to decrease dramatically when the temperature > 475 °C, presumably due to the decomposition of WS$_2$ films. Upon returning to room temperature, the films usually cannot return to the initial states. For the 1L-SiO$_2$ sample, the Raman intensities of the two phonon modes decrease to about half of the initial values; however, their peak positions remain at almost the same position as before, indicating that the bonding between the substrate and film for the CVD-grown samples is fairly robust and not significantly altered by the “annealing” process. For the transferred sample, which is similar to the transferred MoS$_2$ films [27], both Raman intensities and peak positions showed significant changes, indicating that the heating process modifies the bonding between the film and substrate, and thus changes the strain distribution over the film.

3.3 High Temperature Photoluminescence
Lastly we discuss the temperature dependence of PL. Figure 4(a) & (b) show a few representative PL spectra for 1L-SiO$_2$ and 1L-SA-TRI, respectively, and their peak energies are plotted in Figure 4(c). Similar to the trends observed in Figure 3(b) for the $E_{2g}^1(\Gamma)$ Raman shifts, the temperature-dependent PL peak energy shift for 1L-SiO$_2$ has a significant smaller slope than 1L-SA-TRI, due to the relaxation of the built-in tensile strain for the former. The reduced slope for 1L-SA-TRI at very high temperature (> 300 °C) is due to an increasing thermal population at higher states in the bands. The integrated PL intensities are shown in Figure 4(d), showing thermally activated temperature quenching, starting approximately from room temperature. For 1L-SA-TRI, the well-known emission of Cd$^{3+}$ centers from the sapphire substrate has been subtracted. The experimental data can be fit very well with a simple function form below with one activation term for the SiO$_2$ sample ($A_2 = 0$), and two activation terms for the sapphire sample.

$$ I(T) = \frac{I_0}{1 + A_1 \exp(-E_{a1} / k_B T) + A_2 \exp(-E_{a2} / k_B T)} $$

(4)

where $E_{a1}$ and $E_{a2}$ are the activation energies of the thermal quenching processes, $k_B$ is the Boltzmann constant, $I_0$ is the integrated peak intensity at RT, and $A_1$ and $A_2$ are constants. The fitting results are: for 1L-SiO$_2$, $E_{a1} = 0.40 \pm 0.01$ eV; for 1L-SA-TRI, $E_{a1} = 0.20 \pm 0.01$ eV and $E_{a2} = 1.51 \pm 0.06$ eV, respectively, with the fitting curves shown in Figure 4(d). Temperature induced PL quenching in semiconductors typically results from direct or indirect thermal activation of non-radiative recombination processes associated with defects or impurities through emission of phonons. Activation energies as large as these values are unusual, which is largely because PL is rarely performed with temperatures much higher than RT to assess the potential process with such a large activation energy. At this stage, our understanding of defects and impurities in these 2D materials is very limited, thus, speculating upon the physical origins of these thermal quenching
processes is premature. However, we would like to point out an important issue that could be particularly important to 2D materials, that is, the interfacial effect involving carrier exchange between the 2D film and substrate through a thermal activation process. In fact, the magnitudes of the activation energies are comparable to the possible energy barriers between the film and substrate. Theoretical modeling based on first-principle techniques is needed to understand the film-substrate interaction that has yielded the effects reported here for electronic and vibrational properties of 2D materials.

4 Conclusions

In summary, we have performed high temperature, in a range of 25 – 500 °C, Raman and PL studies on CVD-grown epitaxial monolayer WS$_2$ on SiO$_2$/Si and sapphire substrates. The interaction between the 2D film and substrate is shown to depend on substrate type for the as-grown samples and film-substrate bonding between as-grown and transferred samples. At RT, the PL intensity of monolayer WS$_2$ on SiO$_2$ is found to be much stronger than on sapphire substrate under both 532 nm and 441.6 nm excitation. The TEC mismatch between the thin-film and SiO$_2$/Si substrate can generate significant amount of strain after the film is cooled down to RT, manifesting itself as a bandgap shift, strong intensity modification in resonant Raman scattering, and large non-linearity in the temperature coefficient of the vibration mode frequency. The effects are small for the sapphire substrate. These effects associated with the built-in strain are inherent properties of the directly grown 2D films, although this depends upon the specific substrate used. A significant difference exists in the states of the built-in strain between the directly grown and transferred films even on the same type of substrate. The in-plane vibration mode, $E_{2g}^1(\Gamma)$, is more sensitive to the strain effect, whereas the out-of-plane vibration mode, $A_{1g}(\Gamma)$, is more sensitive to the film-substrate bonding or the film morphology. Because of the strong electron-phonon coupling of the
A\(_{1g}(\Gamma)\) mode as dictated by symmetry, a transferred film without proper thermal annealing is expected to have an inferior carrier mobility. The intrinsic temperature coefficients for the \(E\(_{2g}\)\(^1(\Gamma)\) and \(A\(_{1g}\)\( (\Gamma)\) modes in monolayer WS\(_2\) are determined to be: \(\chi(E_{2g}^{1}(\Gamma)) = -0.0142 \pm 2 \times 10^{-4} \text{ cm}^{-1}/\text{K},\) derived from the transferred film on SiO\(_2\); and \(\chi(A_{1g}(\Gamma)) = -0.0130 \pm 9 \times 10^{-5} \text{ cm}^{-1}/\text{K}\) (lower bound), derived from the as-grown film on SiO\(_2\). These values are somewhat smaller than the corresponding ones in MoS\(_2\): \(\chi(E_{2g}^{1}(\Gamma)) = -0.0221 \pm 9 \times 10^{-4} \text{ cm}^{-1}/\text{K},\) and \(\chi(A_{1g}(\Gamma)) = -0.0197 \pm 9 \times 10^{-4} \text{ cm}^{-1}/\text{K}\). For all other cases, the temperature coefficients are affected by the substrate to different extents, but this effect is most severe for the film grown on SiO\(_2\) with \(\chi(E_{2g}^{1}(\Gamma)) = -0.0100 \pm 3 \times 10^{-4} \text{ cm}^{-1}/\text{K}.\) Therefore, temperature-dependent Raman investigations provide an effective tool for investigating the epilayer-substrate interaction. Additionally, high temperature PL studies on monolayer WS\(_2\) have revealed thermal quenching processes with large activation energies of \(E_{a1} = 0.40 \text{ eV}\) for the film grown on SiO\(_2\) and \(E_{a1} = 0.20 \text{ eV}\) and \(E_{a2} = 1.51 \text{ eV}\) for the film grown on sapphire.

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**Electronic Supplementary Material:** Supplementary material (Raman spectrum fitting, PL spectra collected with 532 nm excitation wavelength, Raman spectrum correction of 1L WS\(_2\) on sapphire, and temperature coefficients for all samples fitted with a third-order polynomial function)
is available in the online version of this article at http://dx.doi.org/10.1007/*.*.*.*.*.*.*.*
References


[42] Y. Li, J.-W. W., J.-B. Li, and Y. Zhang (private communication).


Figures and Tables

Figure 1. (a) Schematic model of WS\(_2\) single layer with top and side views. (b)-(e) Optical images of WS\(_2\) samples: (b) 1L-SiO\(_2\) and bulk-SiO\(_2\), (c) 1L-TRAN-SiO\(_2\), (d) 1L-SA-TRI, and (e) 1L-SA-FILM. (f) AFM image of 1L WS\(_2\) triangle on sapphire, with thickness of 0.7 nm.

Figure 2. (a)-(f) Raman and PL of all five WS\(_2\) samples with excitation wavelengths of 441.6 nm (blue line) and 532 nm (green line). (f) PL with 441.6 nm excitation.

Figure 3. (a) Representative Raman spectra of 1L-SiO\(_2\) sample at different temperatures. (b)-(c) Temperature dependence of Raman frequencies of (b) \(E_{2g}^1(\Gamma)\) and (c) \(A_{1g}(\Gamma)\) modes in “bulk” and 1L samples. The solid lines are fitting results using Equation 2, with the temperature coefficients shown in Table S1.

Figure 4. (a)-(b) Representative PL spectra of (a) 1L-SiO\(_2\) and (b) 1L-SA-TRI at particular temperatures. (c) Temperature dependence of PL peak energy for 1L-SiO\(_2\) and 1L-SA-TRI samples. (d) Integral PL intensity of 1L-SiO\(_2\) and 1L-SA-TRI at different temperatures.

Table 1. Relative intensities of Raman and PL of four monolayer WS\(_2\) samples measured by two excitation wavelengths: 532 nm and 441.6 nm. For each column, the weakest intensity serves as unity reference.

Table 2. Temperature coefficients of bulk and 1L WS\(_2\) samples.
Figure 1
Figure 2
Figure 3
Figure 4
<table>
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<th>441.6 nm</th>
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<td>PL</td>
<td>Raman</td>
<td>PL</td>
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</table>
Table 2

<table>
<thead>
<tr>
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<th>$E_{2g}^1(\Gamma)$ (cm$^{-1}$/K)</th>
<th>$A_{1g}(\Gamma)$ (cm$^{-1}$/K)</th>
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<tr>
<td>Bulk</td>
<td>$-0.0124 \pm 2 \times 10^{-4}$</td>
<td>$-0.0136 \pm 4 \times 10^{-5}$</td>
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<td>$-0.0100 \pm 3 \times 10^{-4}$</td>
<td>$-0.0130 \pm 9 \times 10^{-5}$</td>
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<tr>
<td>1L-TRAN-SiO$_2$</td>
<td>$-0.0142 \pm 1 \times 10^{-4}$</td>
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<td>1L-SA-TRI</td>
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<td>1L-SA-FILM</td>
<td>$-0.0155 \pm 2 \times 10^{-4}$</td>
<td>$-0.0143 \pm 6 \times 10^{-4}$</td>
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</table>
Temperature-dependent Raman and photoluminescence up to the decomposition temperature are used to study the interaction between the monolayer WS$_2$ films, either transferred or CVD-grown, and substrates (SiO$_2$/Si and sapphire). The impact of the substrate, particularly the strain and doping effects, is revealed to be sensitive to not only the substrate type but also the material-substrate bonding for the same substrate.