

Investigating the effects of sample-substrate interaction in the Raman and photoluminescence spectrum of 1L-WS₂

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Summary. — We carried out a spectroscopic investigation on monolayer (1L) crystals of WS₂ deposited on different substrates, namely PDMS, silica, gold, hBN, and diamond, by Raman and photoluminescence measurements. Two spectral features were identified, which assess the degree of strain and doping transferred to the 1L-WS₂ flake by the substrate. The first one is the frequency of the E_{2g}¹(Γ) peak in the Raman spectrum, whose blueshift is associated with an increase in the tensile strain applied to the 1L-WS₂ crystal. The second one is the intensity ratio of the trion to exciton band in the photoluminescence spectrum, related to the density of electrons in excess from doping levels. A comparative analysis of the 1L-WS₂ spectra collected on the different substrates reveals that the flakes deposited on diamond are those displaying a higher degree of strain and doping, possibly due to the large presence of C dangling bonds. Our results represent a valuable reference for high-pressure optical measurements on low-dimensional transition metal dichalcogenides, in which 1L flakes are commonly exfoliated on the culet of Diamond Anvil Cells.

1. – Introduction

Transition Metal Dichalcogenides (TMDs) are layered crystals formed by stacking layers with atomic-scale thickness connected through weak inter-layer van der Waals (vdW) interactions. The layered structure of TMDs makes the inter-layer interaction a key parameter governing their physical properties and, in particular, their electronic band structure. A well-known example in this sense is provided by the indirect to direct band gap transition observed in most TMD semiconductors in the passage from bulk to monolayer (1L) crystals [1]. For this reason, semiconducting TMDs have attracted significant attention for their potential application in optoelectronics.

The same VdW forces responsible for the interaction between adjacent layers also govern the interaction with the substrate. The latter can determine strain or doping in the samples, which can modify their vibrational and electronic properties [2, 3]. That effect is particularly relevant in 1L-TMDs due to their nearly all-surface nature.

To investigate the sample-substrate interaction in 1L-TMDs, we performed a Raman and photoluminescence (PL) spectroscopic study of 1L-WS₂ on different substrates, namely PDMS (polydimethylsiloxane), silica, gold, hBN (hexagonal Boron Nitride), and diamond. The position of the E_{2g}¹(Γ) peak in the Raman spectrum was exploited to account for the degree of strain applied on the 1L-WS₂ flake by the substrate, while the intensity ratio of the trion to exciton band in the PL spectrum allowed us to estimate the increase in the density of electrons in excess due to the sample-substrate interaction.

Our results show that the 1L-WS₂/diamond sample exhibits the highest degree of strain and the greatest density of excess electrons among the considered systems.

This study can represent a valuable reference in the context of high-pressure measurements performed by Diamond Anvil Cells [4-6], in which 2D materials are usually exfoliated on diamond culets.

2. – Materials and methods

1L-WS₂ flakes were mechanically exfoliated from their bulk crystal (purchased by HQ Graphene) and transferred on four different substrates: PDMS, silica, hBN, and diamond. An additional 1L-WS₂ crystal, synthesized by molecular beam epitaxy onto an Au/SiO₂/Si substrate, was purchased by 2D Semiconductors.

All samples were characterized through Raman and PL spectroscopy exploiting a Horiba LabRam HR Evolution microspectrometer, equipped with a 532 nm laser, a grating monochromator (with 600 and 1800 grooves/mm for PL and Raman measurements, respectively), and a charge-coupled device detector [7].

3. – Results and discussion

For each 1L-WS₂/substrate sample, we collected the Raman spectrum in the range 250–430 cm⁻¹ in which the most characteristic intra-layer modes are found. Figure 1(a) shows the Raman spectra of 1L-WS₂/diamond, providing an example of the measurements and the data fitting process.

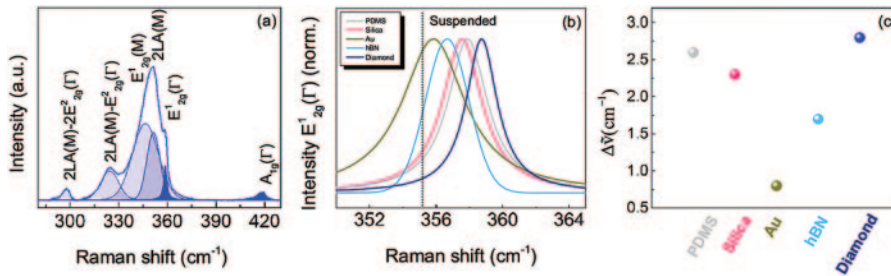


Fig. 1. – (a) Raman spectra of 1L-WS₂/diamond in the range 250–430 cm⁻¹ with an example of the data fitting procedure [8]. The filled-area peaks at ~ 357 and ~ 417 cm⁻¹ correspond to the non-resonant modes E_{2g}¹(Γ) and A_{1g}(Γ). The shaded-area peaks below 350 cm⁻¹ correspond to modes activated by the resonance condition with the laser excitation energy (2LA(M)-2E_{2g}²(Γ), 2LA(M)-E_{2g}²(Γ), E_{2g}¹(M), and 2LA(M)). (b) Normalized fitting curve for the E_{2g}¹(Γ) mode of 1L-WS₂ on the five different substrates. (c) Difference $\Delta\nu$ between the E_{2g}¹(Γ) central frequency of 1L-WS₂/substrate and suspended 1L-WS₂ [9].

Besides the contributions below 350 cm^{-1} assigned to resonant modes [8], the in-plane $E_{2g}^1(\Gamma)$ and out-of-plane $A_{1g}(\Gamma)$ peaks are visible at ~ 357 and $\sim 417\text{ cm}^{-1}$, as shown in fig. 1(a). A fitting procedure with six voigtian functions was carried out to estimate the central frequencies of the Raman peaks at varying the substrate. The obtained results indicate that, while the $A_{1g}(\Gamma)$ position remains practically fixed, the $E_{2g}^1(\Gamma)$ frequency displays a clear substrate dependence, well-visible in fig. 1(b)–(c).

Based on previous results from the literature [9], the difference $\Delta\tilde{\nu}$ between the $E_{2g}^1(\Gamma)$ central frequency of 1L-WS₂/substrate and suspended 1L-WS₂ (355 cm^{-1}) can be ascribed to the different degree of planar strain transferred to the 1L lattice by the substrate. In particular, a compressive strain, which induces a hardening of the in-plane bonds in the 1L crystal, is expected to determine a blueshift of the $E_{2g}^1(\Gamma)$ frequency, while the application of tensile strain results in a redshift of the $E_{2g}^1(\Gamma)$ peak [10]. In the present case, we observe a blueshift in the $E_{2g}^1(\Gamma)$ mode in all the 1L-WS₂/substrate systems considered, with the maximum $\Delta\tilde{\nu}$ measured in the 1L-WS₂/diamond case.

In this framework, the unresponsiveness of the $A_{1g}(\Gamma)$ peak center witnesses the absence of both calibration-dependent frequency offsets in the measured spectra and out-of-plane strain gradients on the 1L-WS₂/substrate systems.

Figure 2(a)–(e) shows the PL spectra of the 1L-WS₂/substrate systems as a function of the laser power. The PL spectrum of 1L-WS₂ is characterized by the presence of two distinct bands: the A exciton (higher energy), originating from the radiative recombination processes through the direct bandgap, and a lower energy contribution ascribable to the recombination of the negative trion T [11]. The latter is a quasi-particle formed by a hole in the valence band and two excited electrons. The probability of trion recombinations increases with the electron density in the conduction band. We thus expect the T

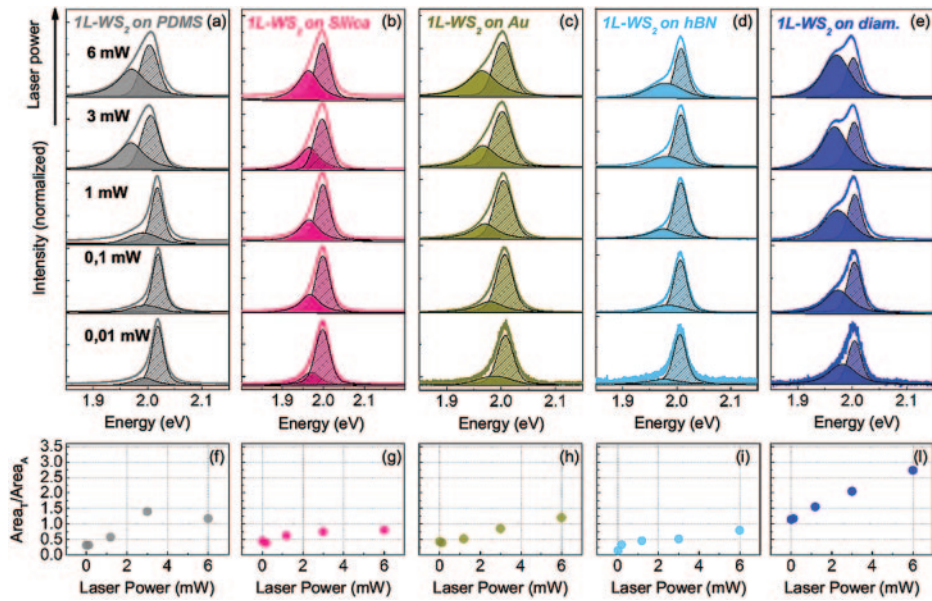


Fig. 2. – PL spectra of 1L-WS₂ on five different substrates: PDMS (a), silica (b), gold (c), hBN (d), and diamond (e). Evolution of the intensity ratio of the trion to exciton band at varying the laser power for 1L-WS₂ on PDMS (f), silica (g), gold (h), hBN (i), and diamond (l).

feature to become more intense in systems with intra-gap states hosting excess electrons that can be easily excited to the conduction band. Based on the previous discussion, the T to A intensity ratio in the PL spectrum of 1L-WS₂ can be exploited as a spectral benchmark to evaluate the increase in the density of excess electrons induced by different substrates [12]. Knowing that the T/A relative intensity displays a marked dependence on the exciting laser power [13], for each 1L-WS₂/substrate system we performed PL measurements on increasing the laser power from 0.01 to 6 mW. Figure 2(f)–(l) shows that at 0.01 mW the T to A area ratio ($\text{Area}_T/\text{Area}_A$) is higher in the 1L-WS₂/diamond sample compared to the other systems, suggesting a larger density of substrate-induced electrons in excess in this configuration probably given by the rough surface of the diamond and the presence of dangling bonds [14]. Remarkably, the $\text{Area}_T/\text{Area}_A$ ratio in 1L-WS₂/diamond becomes even larger on increasing the laser power, with a growth rate of nearly 0.3 mW^{-1} to be compared with the approximately 0.1 mW^{-1} measured for the other configurations; see fig. 2(f)–(l).

4. – Conclusions

Our measurements indicate that 1L-WS₂ crystals exfoliated on diamond undergo the highest degree of tensile strain and display the largest density of electrons in excess among the systems considered. This might be due to the presence of a greater amount of dangling bonds on the diamond surface compared with amorphous substrates, responsible for an enhanced interaction with the overlayer. The obtained results represent a valuable reference for high-pressure optical measurements on low-dimensional transition metal dichalcogenides, in which 1L flakes are commonly exfoliated on the culet of diamond anvil cells.

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