Local Optical Properties in CVD-Grown Monolayer WS$_2$ Flakes

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Supporting Information I
Modelling the laterally-averaged SE data

In order to model the ellipsometry data, we adopted the following strategy. On the same sample considered in the main text, we performed an SE measurement with a J.A. Woollam VASE equipped with focusing probe; then, we adapted the model presented in Ref. [1] to reproduce the experimental data from VASE. Briefly, we used a patented PSEMI dispersion formula (US patent 5,796,983, Aug. 18, 1998, Herzinger et al.) to describe the WS$_2$ optical response, and used a linear Effective Medium Approximation to properly take into account the surface coverage of WS$_2$. In this way, we obtained a model that can satisfactorily describe the “average” optical properties of the WS$_2$ flake described in the main text. In the following, we review in detail each step.

The structure of the model (i.e. number of layers and oscillators) is the same of Ref. [1]. The substrate was measured with SE before the WS$_2$ deposition, and its ellipsometric response was modelled independently with a Cauchy dispersion formula; the amplitude and center position of each oscillator in the WS$_2$ layer was fitted to the VASE data. We fed into the model the actual surface coverage of WS$_2$ in the area probed by VASE, that is, 30% (this value was obtained from the analysis of optical microscopy images), and the WS$_2$ thickness (0.8 nm, obtained from AFM data in Supporting Information IV). Therefore, the model was effectively adapted to describe the specific sample under investigation.

The accuracy of the model was good (MSE=5.4); the experimental and calculated data are compared in Fig. SI1. Indeed, the model reproduces very well the features corresponding to the A and B excitons, while at the higher energies, the accuracy seems to decrease. However, it must be noted that due to depolarization and low intensity on the detector, the experimental datapoints at higher energies have a relatively large uncertainty (at least ±1 in $\Psi$ and ±2.5 in $\Delta$); for this reason, the relative weight of those datapoints within the fitting calculations is smaller, resulting in a higher discrepancy between generated and experimental data.

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**Fig. SI1.** Dotted curves: Experimental $\Psi$ and $\Delta$ measured with VASE; Continuous curves: $\Psi$ and $\Delta$ calculated from the model adapted from Ref. [1].
The validated model allows to generate ellipsometry data that can be compared with the ISE data reported in the main text. There, we calculated SE data by considering a 100% surface coverage of WS$_2$ and 40° angle of incidence, in order to match the conditions in which the ISE data were acquired. From the model, we also calculate the complex dielectric function of monolayer WS$_2$ in the case of 100% surface coverage. In both cases, the analysis on the laterally-averaged SE data provides an “average” reference for the ISE data and local dielectric function.

[1] Magnozzi, M. et al. Optical dielectric function of two-dimensional WS$_2$ on epitaxial graphene. 2D Materials, 7, 025024, 2020.
Supporting Information II

Microscopical characterization of three WS\(_2\) flakes

| Optical microscopy | Imaging Ellipsometry @ 2.0 eV | Imaging photoluminescence spectroscopy |
|-------------------|-------------------------------|----------------------------------------|
| ![Image 1A](image1) | ![Image 1B](image2) | ![Image 1D](image3) |
| ![Image 2A](image4) | ![Image 2B](image5) | ![Image 2D](image6) |
| ![Image 3A](image7) | ![Image 3B](image8) | ![Image 3D](image9) |

**Fig. SI2**: overview of three WS\(_2\) flakes observed with optical microscopy (column A), imaging ellipsometry at 2.0 eV (col. B: \(\Delta\); col. C: \(\Psi\)), and photoluminescence spectroscopy (col. D: peak intensity; col. E: spectral position; col. F: FWHM).
Supporting Information III

IPL data fitting

The PL spectra of monolayer WS₂ on SiO₂ typically exhibit a major peak and much less intense, broader, and redshifted one; they are determined by the neutral excitons and charged excitons (trions), respectively. The two peaks are represented in Fig. SI3 as two Lorentzian functions fitted to one IPL spectrum. In the IPL data of this work, the trion peak was often so small that it became undistinguishable from the background; therefore, only the main peak (neutral exciton) is discussed in the main text.

Fig. SI3. In this IPL spectrum, the trion feature is sufficiently intense to be distinguished from the background.
Supporting Information IV

AFM Data

**Fig. SI4.** AFM height signal from the flake discussed in the main text. A remarkably uniform height was observed on the whole flake, with no multilayer terraces.

**Fig. SI5.** ROI 4 (white rectangle) observed with AFM. The whole ROI is crossed by a crack in WS$_2$ which extends up to the edge of the flake. The inset shows a zoom on the crack.
Supporting Information V

Raman spectra

Representative Raman spectra confirmed that the flake is composed of a monolayer WS$_2$. The Raman spectrum acquired within the top inner triangular region (red dot in Fig. SI6) describes the typical fingerprint of a monolayer WS$_2$, as indicated by the Raman mode $(2\text{LA(M)} + \text{E}_{2\text{g}}^1)/\text{A}_{1\text{g}}$ intensity ratio greater than 5. [2,3] The same spectral pattern is measured on the bisector. In the center of the flake, however, the features depart from those of typical monolayer WS$_2$ ($(2\text{LA(M)} + \text{E}_{2\text{g}}^1)/\text{A}_{1\text{g}} \sim 2$), due to the fact that this region corresponds to the center of nucleation, where structural defects are formed during the growth of the flake. [4]

![Raman spectra](image)

**Fig. SI6.** Raman spectra acquired on the flake discussed in the main text.

[2] Berkdemir, A. et al. Identification of individual and few layers of WS$_2$ using Raman Spectroscopy. *Scientific Reports* 3, 1755, 2013.
[3] Pace, S. et al. Thermal stability and photo-activated degradation of monolayer WS$_2$ in BEOL conditions. *Journal of Physics: Materials*, 4, 024002, 2021.
[4] Cong, C. et al. Optical properties of large-area single-crystalline 2D semiconductor WS$_2$ monolayer from chemical vapor deposition. *Advanced Optical Materials* 2, 131, 2014.