Supplementary Information for: Electronic properties of single-layer tungsten disulfide on epitaxial graphene on silicon carbide

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1 Model systems and DFT calculations

Two different series of DFT calculations were performed: one with the unit cell of WS2 and one for the graphene plus WS2 system using the consensus supercell, namely the (9 × 9) for graphene and the (7 × 7) for WS2, which includes 162+147 = 309 atoms. The initial thickness of the graphene-WS2 system is 8.40 Å (distance between the graphene layer and the top of the WS2 layer), which corresponds to the upper limit suggested by the experimental measurement. All cells and their Brillouin zones are reported in Fig. S1, with the relative location of symmetry points. The cell parameters used are reported in Table 1.

To speed up calculations, we used ultrasoft1 RRKJ2 pseudopotentials combined with a PBEsol3 functional, scalar relativistic for collinear calculations and fully relativistic for spin-orbit calculations. Van der Waals (vdW) corrections were included according to the Grimme scheme4. Convergence checks on energy were performed using the WS2 unit cell (see Fig. S2(a) and S2(b)). A good convergence is achieved at 30 Ry. The density cutoff was set 10 times larger than the wavefunction cutoff in any case. The convergence vs. the k point sampling was also tested (Fig. S2(c) and S2(d)). The final choice was to use a 15 × 15 × 1 grid for the unit cell. For the complete system we performed Γ point calculations, which were proven sufficient for structure convergence in

![Figure S1](image-url)
Table 1 Calculation setup and parameters for the WS$_2$ unit cell and for the graphene-WS$_2$ system

<table>
<thead>
<tr>
<th></th>
<th>WS$_2$ unit cell</th>
<th>Consensus supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.16</td>
<td>22.14</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>25.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Atoms</td>
<td>3</td>
<td>309</td>
</tr>
<tr>
<td>k-points (scf)</td>
<td>15 $\times$ 15 $\times$ 1</td>
<td>1</td>
</tr>
<tr>
<td>Sampling for band calculation (MI KM)</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td>Gaussian smearing (Ry)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Convergence threshold</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Spin treatment</td>
<td>Collinear</td>
<td>Collinear</td>
</tr>
</tbody>
</table>

our previous calculations for smaller supercells$^5$. The band structure was evaluated on a sufficiently dense set of points along the main symmetry directions. In order to compare the isolated WS$_2$ bands with those of the combined system and with the experiment, an unfolding procedure was applied to the band calculations of the latter, using the method developed by Popescu and Zunger$^6$. For each supercell state, defined by $k$ point and band index, the spectral weight, namely the probability of finding a set of states of the unit cell contributing to the supercell state, is calculated. Then for each point in the unit cell $k$-energy space, the spectral function is calculated averaging the contribution of all supercell $k$ points that belong to the same symmetry class. This yields a blurred plot of the band structure. The code used is part of the Quantum ESPRESSO project$^7$. The remapping of points upon refolding is illustrated in Fig. S1(c).

Beside the neutral supercell system, the n-doped system was studied to emulate the polarization effect of the SiC substrate. A negative charge of 0.5 electrons per supercell, corresponding to $\sim 10^{13}$ cm$^{-2}$ and a shift of 15 meV of the Dirac point and 122 meV of the WS$_2$ bands, was added to the cell, while a compensating positive background charge was added to restore charge neutrality.
2 Calculations results

Structural optimization was performed both without and with the vdW corrections, with convergence thresholds of \(10^{-3}\) a.u. for forces and \(10^{-4}\) Ry for the total energy. For the unit cell, the relaxed WS\(_2\) layer has a thickness of 3.12 Å and the W-S bond length is equal to 2.40 Å. The graphene-WS\(_2\) relaxation gives almost the same thickness of the WS\(_2\) layer (3.11 Å) and a negligible change in the bond lengths (within \(10^{-3}\) Å). However, the system thickness depends on the vdW corrections: when they are present. The optimized graphene-WS\(_2\) distance is 3.14 Å from graphene to the bottom of WS\(_2\) and 6.25 Å to the upper side of the WS\(_2\) layer, while in absence of vdW corrections, the configuration remains basically the starting one, namely with 5.11 Å of interlayer distance and 8.35 Å of total thickness. WS\(_2\) and graphene layer energies were also calculated separately, with the same structures of the relaxed full system, in order to evaluate the van der Waals interaction energy between the layers, which results to \(~240\) meV per superficial S atom (i.e. half of the supercell S atoms), or equivalently \(~72\) meV per C atom with vdW corrections. The van der Waals interaction energy evaluated in the experimental structure is lower, namely \(~50\) meV per superficial S atom and \(~15\) meV per C atom.

The band structure was evaluated in the isolated WS\(_2\) unit cell and in the interacting graphene-WS\(_2\) system, in the neutral and doped, vdW corrected and uncorrected system. The band structure of all the evaluated cases is reported in Fig. S4. The comparison between the bands without vdW correction and larger thickness (Fig. S4(a)) and those with corrections and smaller thickness (Fig. S4(c)) shows an average \(~0.4\) eV upward shift of the filled band system and \(~0.6\) eV of the empty bands, and a \(~4\) meV gap opening at the K-point which can be attributed to the stronger interaction between the two layers in the latter configuration. The additional doping (Fig. S4(e)) produces a shift of the Dirac point of 15 meV (inset in Fig. S4(e)). Fig. S4(b), S4(d) and S4(f) show that the increased van der Waals interaction produces an upward shift of \(~120\) meV of the WS\(_2\) bands with respect to the graphene bands, while the effect of doping seems negligible.

2.1 Orbital character of the valence band

In this section we show the projection of the WS\(_2\) wave functions onto the different p and d orbitals along the high-symmetry paths in \(k\)-space to highlight the orbital character of the valence band as a function of \(k\). The composition of the electronic states of the WS\(_2\) unit cell (modelled without substrate) was also analyzed by projecting the wave functions \(\psi_v(\vec{k})\) onto the atomic orbitals (evaluated with the same DFT calculation setup). The projection along each band \(E(\vec{k})\) is

\[
P_i(\vec{k}, E) = \sum_v \sum_j c_{ijv}(\vec{k}) c_{iv}(\vec{k}) S_{ij} \delta \left( E - E_v(\vec{k}) \right),
\]

\(i\) being the atomic orbital index, \(c_{iv}(\vec{k})\) the expansion coefficient of the electronic state onto the atomic orbital basis and \(S_{ij}\) the overlap matrix between atomic orbitals. The atomic orbitals are 17 for W (namely two s states, three p states, five d states and seven f states) and 8 for S (the 3s and the 3p states for each of the two S atoms). In the plot, the following combinations are reported, obtained summing contributions with given symmetry with respect to the z axis

\[d_{x^2-y^2} + d_{z^2}, \text{ sum of W d orbitals with } m = -2 \text{ and } m = 2.\]
Figure S4 Energy bands of the different models: (a)-(b) optimized without vdW corrections, (c)-(d) optimized with vdW corrections and (e)-(f) with doping. Bands (a)-(c)-(e) are the consensus supercell, while (b)-(d)-(f) are those obtained upon unfolding to compare with experiment. The bands of the WS$_2$ unit cell are superimposed as red lines, manually aligned to the unfolded interacting system top of valence band of gamma point located at 1.47 Å$^{-1}$.

- $d_{xz} + d_{yz}$: sum of W d orbitals with $m = -1$ and $m = 1$.
- $d_{z^2}$: W d orbital with $m = 0$.
- $p_{x,y}$: sum of W and S orbitals with $m = -1$ and $m = 1$.
- $p_z$: sum of W and S orbitals with $m = 0$. 
Figure S5 d (left) and p (right) composition of electronic states of WS$_2$ (unit cell) atomic orbitals, evaluated as specified in the text. The size of symbols is proportional to the numerical value of projection.

3 ARPES raw data

In this section we show the ARPES spectra of Fig. 2 without the superposition of calculated bands. Fig. S6(a) is the same as Fig. 3(a). The high symmetry points used as labels for panels (a,b,f,g) refer to the graphene's BZ. In panel (c), the graphene's $\pi$-bands $\mu$ARPES measurement at 27.5 eV is shown. In panel (d) the DFT bands calculated over the single graphene u.c. are shown. Panel (e) correspond to the raw ARPES data shown in Fig. 2(e), acquired with the laboratory setup at the MPI in Stuttgart (see section 2.1 in the paper for details). Panels (f) and (g) are the Fermi surface recorded with $\mu$ARPES on a WS$_2$/MLG crystal for photon energy 70 eV and 27.5 eV, respectively. In panel (f) graphene replica bands are visible. The reciprocal lattice vectors that generate those replicas are the well known 1/6 of SiC ($6\sqrt{3}\times6\sqrt{3})R30^\circ$ reconstruction and the WS$_2$ (10) vector.
4 WS$_2$ spin-orbit splitting in $\overline{K}$

In this section we show the ARPES single spectrum measured in $\overline{K}$ as indicated in the inset of Fig. S7 with He I light. On the right side of the panel, the line intensity profile of the spectrum is shown. The profile is obtained by integrating the intensity of the spectrum about zero, on a region of ±0.025 Å$^{-1}$. The line profile was fitted with four Voigt components. The two at lower binding energies are attributed to bilayer WS$_2$, as also visible from Fig. 1(b).

5 X-Ray Photoelectron Spectroscopy Data

This section is aimed to show the laterally averaged photoelectron spectroscopy data, acquired with a Al-K$_\alpha$ source as described in the 2.1 section in the main text with a photon beam spot of 2×3 mm$^2$ in size. The C 1s and Si 2p spectra (panels (a) and (b), respectively) do not show any peculiar feature deviating from the results expected from a MLG/SiC(0001). The W 4f peak confirms the XPEEM measurements shown in Fig.4(e) of the main text. Here, the WO$_3$/WS$_2$ components ratio is slightly higher, indicating a possible inhomogeneity in the WO$_3$ concentration throughout the sample. Given the higher surface sensitivity of the XPEEM at lower photon energies compared with the XPS, it could also indicate that the WO$_3$ is actually underneath the WS$_2$ and not on top. However, its contribution remains very little. The sulphur component was fitted with a single Voigt doublet in this case as well, as it was the XPEEM peak shown in Fig.4(d).
Overview on the growth of WS\textsubscript{2} on epitaxial graphene

The growth of WS\textsubscript{2} on graphene is a reliable and reproducible technique. It depends critically on the reagents ratio, carrier gas flux (Ar in our case), temperature and distance substrate-WO\textsubscript{3} as described in Ref. [8, 9]. In particular we observe that the WS\textsubscript{2} coverage with respect the graphene area decreases turning away the substrate from the WO\textsubscript{3} powder. Moreover an over sulfurized environment ensures to avoid the formation of any unwanted byproduct such as WO\textsubscript{2}, which forms 3D cluster. Therefore the optimal ration WO\textsubscript{3}:S is 1:100. When byproducts are taken into account also the Ar flux is important since only a sufficient high vapor pressure enables mixing of atomic gases in the right stoichiometry, which are subsequently transported to the substrate. However, the total built-in pressure in the chamber influences the nucleation density. In particular passing from 0.5 to 5 mbar, we can distinguish a higher and a lower nucleation density respectively. The first leading to a continuous large-scale polycrystalline sub-μm size epitaxial film and the second to a ∼ μm size well isolated crystals. Temperature is another parameter that limits the reaction process. If the temperature is too low a polycrystalline film with sub-μmeter grain size will form since adatoms will not have enough kinetic energy to diffuse and find the lowest potential energy site. On the other hand if it is too high the surface diffusion will be fast enough to let molecules deposit on the energetically most favorable places and results in a 3D island growth, or in the worst case leading to the desorption of the molecules from the substrate.

![Figure S9](image.png)

**Figure S9** Picture of the oven and reactor used for the growth. Main parts are indicated with arrows.

References