Scanning tunneling spectroscopy of van der Waals graphene/semiconductor interfaces: absence of Fermi level pinning

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A. STM Experiments on transferred WSe$_2$ flakes

Few-layer WSe$_2$ flakes were exfoliated from a bulk crystal and transferred using polydimethylsiloxane (PDMS) stamps onto graphene films epitaxially grown on SiC(0001) substrates. In order to position the STM tip above the flake of interest, two 30 nm thick Ti/Au markers were evaporated through a mechanical mask on the bare Gr/SiC surface (figure S1a)). These markers are visible under a binocular, and facilitate the STM tip approach to the few tens of micrometers large flake deposited in between them.

We show in figure S1b) a typical 1 x 1 $\mu$m$^2$ STM image of such a WSe$_2$ flake. The edge of the flake (the dashed line) can be seen in the image. From the topographic profile recorded along a line crossing this edge, we deduce an apparent thickness of the flake of about 2 nm, corresponding to a tri-layer (3L) flake (the expected value is 1.9 nm for 3L-WSe$_2$, but a slight difference between these two values is due to the different electronic structures of Gr and WSe$_2$). Furthermore, some bubbles (pointed by arrows) can be seen as protrusions (with apparent height up to 10 nm) on the WSe$_2$ region, as already observed on thin TMD samples prepared by exfoliation techniques [1, 2]. As discussed in these references, such bubbles correspond to protruding parts of the flake which do not adhere to graphene, presumably due to trapped impurities between the flake and the substrate. These contaminants are probably left after the in-air mechanical exfoliation. Noticeably, the WSe$_2$ flake sticks perfectly well onto the substrate away from such bubbles, with a clean interface between the flake and the substrate. Indeed, as exemplified in figure S1b), the steps of the pristine Gr/SiC substrate remain visible on the image even when covered by the 3L-TMD flake (i.e. the flake conforms to the substrate as a carpet).
Figure S2. Identification of the local graphene thickness below the 3L-WSe<sub>2</sub> flake, at the spot shown in figure 1 of the MS. a) The same image as figure 1 a) of the MS: 240 x 65 nm<sup>2</sup> constant current STM image taken close to the edge of the 3L-WSe<sub>2</sub> flake shown in figure S1 (sample bias: -2.0 V, tunneling current: 0.14 nA). The green arrow points towards the edge of the TMD flake. The rectangular blue box indicates the terraces where the dI/dV spectra have been recorded, mostly on A and B terraces, in order to obtain the averaged spectra shown in figure 1 c) of the MS. b) Height profile measurement performed along the pink line drawn on a). c) 240 x 140 nm<sup>2</sup> STM image (sample bias: +1.5 V, tunneling current: 0.15 nA) obtained after accidentally removing part of the flake during the scan. The blue rectangular box corresponds to the boxed region of a), but here without the 3L-TMD. d) (dz/dx) STM image taken at sample bias -0.5 V of the green boxed region shown in the panel c), revealing pristine single-layer graphene (SLG) or bilayer graphene (BLG) terraces (see the text). All the measurements of this figure were obtained at room temperature.

B. STM identification of the local graphene thickness below the 3L-WSe<sub>2</sub> film shown in figure 1 of the MS

This section is devoted to the description of the stacking configuration between the WSe<sub>2</sub> flake and the Gr/SiC substrate which is sketched in figure 1a) and b) of the main manuscript (MS). Indeed, it is mandatory to know the precise number of graphene layers below the A and B regions (figure 1 a) and b)) of the flake where the spectroscopic measurements have been performed. Figure S2 a) is identical to figure 1a) of the MS, but we have added in figure S2 b) a height profile z(x) (recorded along the pink line sketched in figure S2 a)) which gives the apparent height of the different steps along the profile. In particular, the step with a height of 1.9 nm at the far right of the profile corresponds to the edge of the WSe<sub>2</sub> flake, as expected for such a homogeneous flake. Two other steps along the profile exhibit a 0.75 nm height, i.e. three times the distance (0.25 nm) between two neighbouring Si-C layers in bulk SiC(0001). This indicates that the number of graphene layers (below the TMD) is the same on the left and right terraces separated by such steps. However, the profile also shows a step of apparent height 0.39 nm, which is not an integer multiple of 0.25 nm. Thus, the graphene thickness below the TMD film changes when crossing such a step, and this finding will be confirmed next.
After performing the topographic and spectroscopic measurements reported here and in figure 1 on the MS, the tip has accidentally removed a portion of the WSe$_2$ flake, while scanning laterally. We know that such event sometimes takes place while crossing the edge of the TMD flakes, depending on the tunneling setpoint and on the scan speed. In consequence, as shown in figure S2 c), the bottom part of the flake (in and around the green boxed region) has been ripped off, revealing the pristine Gr/SiC terraces, whereas the upper part of the flake still remains undamaged.

Figure S2 d) displays the $(dz/dx)$ derivative of a low bias ($-0.5$ V) STM image corresponding to the green boxed region of figure S2 c). This derivative image enhances the apparent height corrugation of the distinct terraces, labeled SLG (resp. BLG) where the corrugation is high (resp. low). As explained in MS, such a corrugation, which roughly forms a triangular pattern of period 1.9 nm, arises from the interface states of the buffer layer separating the first graphene layer from the SiC substrate [3, 4, 5]. The contribution of such states to the tunneling current is higher when the tip stays above single-layer graphene than above bilayer graphene, because of the different tip/buffer layer distance between these two configurations. Since single and bilayer graphene are by far the dominant phases on our sample, we conclude that regions labeled SLG (BLG) are single-layer (bilayer) graphene.

Finally, we draw in figure S2 c) a rectangular blue box corresponding to the blue boxed region of figure S2 a), indicating once again the area where the STS measurements of figure 1 c) were performed. Of course, in figure S2 c) the 3L-WSe$_2$ film is missing, but from the arguments given above, it becomes obvious that the terraces labeled A and B in figure 1 a) and figure S2 a) correspond to 3L-WSe$_2$/SLG and 3L-WSe$_2$/BLG respectively.

C. Experiments performed on another region of the 3L-WSe$_2$ flake covering SLG/BLG substrates

Because of the large size of the transferred flake, it covers many SLG-BLG steps. We are thus able to study the influence of SLG and BLG on the electronic structure of the 3L-WSe$_2$ flake at various locations, although the direct identification of the underlying graphene phases is only possible at the edges of the flake. For instance, figure S3 exhibits STM/STS results obtained on another place of the same flake with another STM tip. These d$I$/d$V$ spectra are very similar to those of figure 1 c). They show the same bandgap ($\sim 1.5$ eV) and bumps in a quite similar bias range (from $-1.6$ V to $-1.7$ V). Moreover, two minor structures appear at smaller negative biases ($-1.14$ V and $-1.28$ V for spectra obtained on WSe$_2$/BLG and WSe$_2$/SLG respectively). Similar features are also observed in the experiments reported in [6] for 3L-MoSe$_2$/BLG and they correspond to maxima of the valence band at the $\Gamma$ point (they are more visible here than in the data presented in figure 1 of the MS due to the use of a log-scale and a better signal-to-noise ratio).

Similar to what we did in figure 1 c), a shifted spectrum corresponding to the curve with orange circles in figure S3 is obtained by multiplying the blue curve by a factor of three and then by performing a bias-shift of $+110$ mV. Again we find a good match between this modified 3L-WSe$_2$/SLG curve and the raw spectrum obtained on 3L-WSe$_2$/BLG, which confirms the sign and the value of the shift deduced from figure 1 of the MS.
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**Figure S3.** STM/STS measurements of another part of the 3L-WSe$_2$ transferred flake supported by SLG and BLG: a) STM image ($V_b=1.3$ V, $I_t=1.0$ nA) of a region, where the WSe$_2$ flake covers SLG (the left and bottom part) and BLG (the right and top part) terraces. A series of dI/dV spectra are recorded along the black line crossing the SLG-BLG step. A topographic profile along this line is shown in the inset. b) Spatially averaged dI/dV curves (blue and red solid lines) measured on WSe$_2$/SLG and WSe$_2$/BLG at room temperature. Each curve is an average of 20 (essentially identical) spectra recorded at different points. Orange circles are obtained by resizing and shifting (signal x3, +135 mV) the blue curve to overlap it with the red one (see the text).

**Figure S4.** Investigation of the tip-induced band-bending: a) dI/dV spectra consecutively obtained at a single position on 3L-WSe$_2$/SLG with $V_b=-2.2$ V for all curves and various $I_t$ values (0.2 nA, 1 nA and 5 nA). In order to take into account the different setpoints values, the lock-in sensitivity was changed between each spectrum. No bias-shift is applied in the figure. b) The bias dependence of the difference in height, $\Delta z$, between WSe$_2$/SLG and WSe$_2$/BLG terraces (shown in the inset). These $\Delta z$ values are extracted from a series of successive STM images taken on this region with different biases, but with the same tunneling current ($I_t=0.2$ nA).

**D. Study of the tip induced band-bending on the 3L-WSe$_2$ sample**

The tip induced band-bending (TIBB) is a well-known effect in STM/STS studies of semiconductor surfaces [7]. It consists in a local gating effect of the polarized tip on the semiconductor surface. As a result, only part of the nominal sample bias $V_b$ is actually applied between the tip and the sample surface. The remaining part of $V_b$ drops between the surface and the bulk of the semiconductor, creating a local band-bending...
in the sample below the tip. TIBB will thus make the measured band structures of semiconductors shift with respect to the genuine ones (i.e. without the tip). The amplitude of this effect depends on many factors such as the tip characteristics (its radius and work function), the tunneling parameters (the tip-sample distance and $V_b$), the doping level of the semiconductor and the presence of surface states [8].

For the purpose of this paper, our concern is to know how much a difference in TIBB for TMD flakes residing on SLG and BLG substrates could contribute to the extracted shift. The reason is that a difference of about 100 meV in TIBB for STS measurements performed on TMD/SLG and TMD/BLG can lead to an incorrect interpretation of our results. Then, the difference in TIBB rather than their absolute values is essential. In the following, we argue that this difference in TIBB is indeed small and has only a marginal impact on the measured shift. Only the results for the case of the 3L-WSe$_2$ sample measured at room temperature will be discussed here (although we have obtained similar results for the 1L-MoSe$_2$ sample at low temperature) because of two reasons. Firstly, the 3L-WSe$_2$ flake is the thickest among the two studied samples, and is thus the most likely to exhibit significant TIBB. Secondly, since Ugeda and collaborators have reported a negligible TIBB for 1L-MoSe$_2$ on BLG [9], the difference in TIBB due to SLG/BLG substrates should also be insignificant.

In our comparative STS measurements of 3L-WSe$_2$ on SLG and BLG, we tried to avoid such a difference in TIBB by analyzing only spectra (shown in figure 1 c) or figure S3 b)) taken using identical tunneling setpoint ($I_t$, $V_b$) and with the same tip (its radius and work function). Moreover, the studied semiconducting material has the same characteristics (doping levels) on the two substrate phases. However, a difference in TIBB may still occur between the two cases because the tip-sample distance is actually different for the TMDs residing on SLG and BLG for a given tunneling setpoint. This is illustrated in figure S4 b), which shows the bias dependence of the apparent height of a step separating TMD/SLG and TMD/BLG terraces, as noted. Here, the TMD/SLG terrace is higher (brighter) than the TMD/BLG one. The identification for these terraces was achieved from the local STS spectra, where a bias-shift similar to those presented and discussed in figure 1 and in figure S3 exists. Due to the downward shift of the band structure for TMD/SLG relative to TMD/BLG, more (resp. less) states are available for tunnelling at $V_b > 0$ (resp. $V_b < 0$) on TMD/SLG than on TMD/BLG. Consequently, the tip-sample distance at a given setpoint will be larger (resp. smaller) for TMD/SLG than for TMD/BLG for $V_b > 0$ (resp. $V_b < 0$). This results in a larger apparent height of the step for $V_b > 0$ than for $V_b < 0$, as presented in figure S4 b). The difference between the mean apparent heights for $V_b > 0$ and $V_b < 0$, which is 0.07 nm from figure S4 b), provides the maximum value of the variation in the tip-sample distance between TMD/SLG and TMD/BLG for a given setpoint.

Now, we show that such a change in the tip-sample distance induces only a slight modification in the tunneling spectra of the TMD. Figure S4 a) shows a series of $dI/dV$ curves recorded at the same position on 3L-WSe$_2$/SLG for increasing setpoint tunneling currents $I_t$ at a given setpoint bias ($V_b = -2.2$ V). This corresponds to a total variation in the tip-sample distance by 0.13 nm between $I_t = 0.2$ nA and $I_t = 5.0$ nA, as deduced from the exponential $I(z)$ curve measured at this position at $V_b = -2.2$ V. Hence, an increase (resp. decrease) of the tip-sample distance by about 0.07 nm is responsible for the reduction (resp. raise) of $I_t$ from 1.0 nA to 0.2 nA (resp. 5.0 nA). These changes in the tunneling setpoint only have a minor impact on the position of
Figure S5. STM/STS measurements of another MoSe₂ flake supported by SLG and BLG substrates: a) A STM image (Vₜ=1.3 V, Iₜ=50 pA) of a MoSe₂ flake residing on SLG (top) and BLG (bottom) terraces. b) A zoomed-in image (8 x 8 nm²) of the bare SLG/BLG substrate step (Vₜ=0.5 V, Iₜ=50 pA). Hexagonal and triangular atomic patterns, belonging to SLG and BLG terraces [4], are visible.

the structures in the spectra as presented in figure S4 a). For instance, the position of the main peak of the VB at −1.68 V for Iₜ=1.0 nA only shifts by −15 mV (resp. +15 mV) when Iₜ changes to 0.2 nA (resp. 5.0 nA). This number is one order of magnitude smaller than the shift measured at a given setpoint between TMD/SLG and TMD/BLG, and, as quoted above, 0.07 nm is a maximum value for the variation of the tip-sample distance between the two cases. Thus, the difference in TIBB influences only marginally the value of the shift given in the main paper. This is confirmed by similar values of the shift extracted from spectra (not shown) taken on the left (WSe₂/SLG) and right (WSe₂/BLG) terraces shown in the inset of figure S4 b) at positive (Vₜ=+1.25 V) and negative (Vₜ=−2.0 V) bias setpoints.

E. Experiments performed on another 1L-MoSe₂ flake at 8.5 K

Figure S5 presents STM images obtained on another single-layer MoSe₂ flake covering SLG and BLG substrates, which correspond to the top and bottom terraces in the panel a). Hexagonal and triangular patterns seen in atomically resolved STM images in panel b) are fingerprints of the two different graphene phases. Then, we performed again a series of STS spectra along a line indicated by the black arrow in figure S5 a), going from the higher terrace to the lower one. These spectra are presented in the color-coded dI/dV map in figure S6 a). As can be seen, unlike in the data shown in figure 3 a), there are regions marked with dashed vertical lines and white arrows, where significant band-bending and/or in-gap states exist. Smaller scale images of the corresponding areas (not shown) reveal twin boundaries, which are reported to generate in-gap states and band-bending [10]. However, by analyzing spectra recorded far away from these regions, we can estimate the band shift due to the influence of different underlying substrates.

For this purpose, we again average STS spectra measured at 10 neighbouring points for each terrace (SLG and BLG). These points are kept far enough from twin boundaries, so that STS curves are identical (neither band-bending nor in-gap states are found). These averaged spectra are presented in figure S6 b) as red and blue curves (for MoSe₂/BLG and MoSe₂/SLG, respectively). Then, the alignment procedure for
Figure S6. STM/STS measurements of another MoSe$_2$ flake supported by SLG and BLG substrates: a) A color-coded d$I$/d$V$ spectra obtained along the arrow in figure S5a. Dashed lines and two-headed white arrows indicate regions, where band-bending due to defects exist. b) Spatially averaged STS spectra taken on A and B regions of a) (the red and blue curves respectively). The new “shifted” curve with open orange circles is obtained by resizing the blue curve (signal x2.2, +135 mV).

these two spectra is performed as described in MS (and in section C above) and results in the shifted curve displayed with orange circles. The matching of the red curve (bare MoSe$_2$/BLG spectrum) with the orange one (shifted MoSe$_2$/SLG spectrum) is quite good for a value of the shift of +135 mV. Thus, for this region, the value of the shift is again essentially equal to the difference in work function for the bare BLG and SLG substrates.

F. The use of the Schottky-Mott model:

One crucial point when discussing the validity of this model is that the electronic states of the metal and semiconductor should not be drastically modified at the interface when the materials are put into contact (see [11]). We present below some arguments to support this statement for either the TMD or the supporting SLG and BLG substrates.

**TMD flakes:** The band structure of the TMD flakes should not be much affected when being brought in contact with the two different graphene phases, otherwise the value of the electronic affinity, $\chi$, could not be regarded as identical on SLG and BLG as in figure 4 in the MS. Considering the similarity between the shapes of the STS spectra taken for the TMDs on SLG and BLG (evidenced by the “shifted” curves in figures 1, 3, S3 and S6) we believe that this is indeed the case. Additionally, ARPES data have shown that the graphene and TMD bands remain uncoupled close to the VBM [12, 13, 14].

**Supporting graphene substrate:** We cannot probe directly the electronic structure of graphene buried below the TMD layers by means of STS. However, those graphene states remain visible in angle resolved photoemission spectroscopy (ARPES) experiments. Such measurements performed on either MoSe$_2$/BLG [12] or MoSe$_2$/SLG [14] (SLG and BLG were also grown on SiC(0001) in these works) demonstrate that the electronic structure of the graphene layer remains essentially unchanged close to the Fermi level. The Dirac cones are preserved with the same
Fermi velocity and, importantly, the doping level of graphene does not change for these TMD/graphene vertical stacks (compared to bare graphene phases). Essentially similar results were obtained for the “reverse” system consisting of a graphene layer reported on either monolayer [15] or bulk TMD substrates [13]. Since the contact between graphene and TMD layers does not affect much the electronic structure of graphene, we believe that the work functions of the bare SLG and BLG phases (and their difference) remain meaningful quantities for the graphene/TMD interfaces.

Reference


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