2D Materials

PAPER

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

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Abstract

We have investigated the electronic properties of two-dimensional (2D) transition metal dichalcogenides (TMDs), namely trilayer WSe2 and monolayer MoSe2, deposited on epitaxial graphene on silicon carbide, by using scanning tunneling microscopy and spectroscopy (STM/STS) in ultra-high vacuum. Depending on the number of graphene layers below the TMD flakes, we identified variations in the electronic dI/dV(V) spectra measured by the STM tip: the most salient feature is a rigid shift of the TMD spectra (i.e. of the different band onset positions) towards occupied states by about 120 mV when passing from bilayer to monolayer underlying graphene. Since both graphene phases are metallic and present a work function difference in the same energy range, our measurements point towards the absence of Fermi-level pinning for such van der Waals 2D TMD/graphene interfaces.

1. Introduction

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) 2H-MoX2 and 2H-WX2 (X = S, Se) have attracted a lot of attention in the last few years. Like graphene, they can be obtained as single-layer or few-layer crystals either by mechanical exfoliation [1] or by a direct growth on various substrates [2–5]. Among their peculiar electronic properties [6], the interest for these materials derives from the existence of a large electronic bandgap (about 2 eV wide) which allowed the demonstration of field effect transistors with a large on-off ratio [7, 8]. Moreover, since the gap is generally direct for single-layer TMDs [9, 10], they can be used as active layers in optoelectronic devices [2, 5].

The realization of complex heterostructures with clean interfaces [11] by vertically stacking 2D materials with various electronic structures (e.g. graphene as a (semi)metal, TMDs as semiconductors and h-BN as an insulator) offers even more flexibility for designing original devices (see [12, 13] for reviews). The adjacent layers of these materials are held together by the (relatively) weak van der Waals (vdW) interaction. In these vdW heterostructures, graphene layers generally act as a conductive (and transparent) electrode to inject or to collect electrical charges. When used in conjunction with TMDs layers, the relevant parameter is thus the Schottky barrier (or band offset) existing at the TMD/graphene interface. Two different limits are desirable: a low barrier height to form ohmic contacts [14, 15] or a significant (but tunable) one for tunnelling devices, as demonstrated in [16] and [17]. In these works, the barrier height could be modulated by external gating [15, 16, 18]. This has been ascribed to the tunability of the Fermi level and work function of graphene [19]. However, a direct characterization of the band offset at TMD-graphene interfaces remains relevant for a detailed understanding of this issue. This question can be addressed by using scanning tunneling microscopy/spectroscopy (STM/STS), which can probe the band edges of the TMD with respect to the Fermi level of graphene on defect-free areas of the sample [20]. This approach complements angle resolved photoemission...
spectroscopy studies [21–23], which demonstrate that the Dirac cones of graphene remain essentially unperturbed when brought in contact with TMDs layers.

In this paper, we present experimental results obtained with STM/STS on thin TMD films (MoSe₂ and WSe₂) deposited on graphene layers epitaxially grown on SiC(0001) substrates. The graphene growth was intentionally controlled to exhibit terraces with either single-layer graphene (SLG) or bilayer graphene (BLG) to investigate the influence of the electronic properties of these substrates on the band offset at the TMD-graphene interface. To ascertain that our results are valid for a broad range of experimental systems, we have considered TMD layers of different thickness (1 and 3 layers) and of different origin: either prepared by mechanical exfoliation or directly grown by molecular beam epitaxy (MBE). Regardless of the chemical composition of the TMD, we systematically observe that STS spectra measured on TMD flakes supported by SLG are shifted in energy with respect to those obtained on flakes residing on BLG. Both the direction and the magnitude of this shift are consistent with the difference in the work function measured on bare SLG and BLG terraces on SiC(0001) substrates [24–27]. This finding provides evidences for the absence of Fermi level pinning at the TMD-graphene interface, as predicted in a recent theoretical work [28]. Consequently, our work suggests that the so-called Schottky-Mott rule [29, 30] may indeed apply to these vdW graphene-TMD heterojunctions [28, 31]. This is at variance with the situation encountered in junctions between TMD materials (MoS₂) and bulk (3D) metals, like Pt, Au, Ni, etc where a strong Fermi level pinning is observed [31]. Incidentally, we do not find evidence in our TMD flakes for the Fermi level pinning by an impurity band reported in samples from different origin [32].

2. Methods

Epitaxial graphene (Gr) was grown on 6H-SiC(0001) substrates via a graphitization process in ultra-high vacuum (UHV) at temperature above 1200 °C, as reported in [33–35]. For the WSe₂/Gr sample, we first equipped the graphitized SiC substrate with Ti/Au alignment markers defined by means of clean electron beam evaporation through a narrow slit intersected by a wire of 150 μm diameter in order to optically locate the transferred flake. Such a flake was mechanically exfoliated from a bulk WSe₂ crystal onto a polydimethylsiloxane stamp and then deterministically transferred on the Gr surface in between the Ti/Au markers with the use of an all-dry technique similar to that described in [36]. Due to the need for a good optical control of the tip location, the experiments on the transferred flake could be performed only in our room temperature STM setup.

For the MoSe₂/Gr sample, we deposited 0.4 monolayer of MoSe₂ using molecular beam epitaxy (MBE) on a second graphitized SiC substrate. The same fabrication process was demonstrated in [37]. An additional Se film was then deposited to protect the MoSe₂ layer against any possible contamination during the exposure to air. Then, the sample was transferred into the UHV preparation chamber connected to a homemade cryogenic STM operating at 8.5 K. The capping Se layer was removed by annealing the sample at 400 °C (at a base pressure 5 × 10⁻¹⁰ mbar), following [20], prior to the STM experiments.

Spectroscopic measurements were performed using the standard lock-in technique: for STS experiments done at 8.5 K, a bias modulation (amplitude 10 mV peak-to-peak, frequency 477 Hz) was added to the dc sample bias in order to extract the dI/dV(V) signal. For STS experiments performed at 300 K, the amplitude and frequency modulation were 40 mV and 7 kHz. Each dI/dV(V) spectrum was recorded while ramping the sample bias, with the feedback loop open. In between two successive spectra, the feedback loop was closed using the stabilization parameters (sample bias, setpoint current) given in the text. To ensure the high quality of our data, we systematically performed I(ε) measurements to verify that the tunneling regime is guaranteed. Only data taken in defect-free areas of the sample were analyzed since it has been shown that defects, such as edges [38, 39], or twin boundaries [40] can induce locally in-gap states and rigid shifts of the band edges in the TMD layers (see an example in section E of the supplementary information- SI) (stacks.iop.org/TDM/4/035019/mmedia). All the measurements were performed using mechanically etched PtIr tips. The data were analyzed by using the WSXM software [41].

3. Results

We start with STM/STS measurements performed on a few-layer thick WSe₂ flake transferred on a graphitized silicon carbide Si-face wafer (see Methods). Basically, such a substrate provides terraces of sizes 30–60 nm with either single-layer graphene (SLG) or bilayer (Bernal stacked) graphene (BLG). The graphene layers are separated from the underneath SiC by a so-called carbon buffer layer, well documented in the literature [33, 42, 43]. Furthermore, epitaxial graphene on SiC substrates is heavily n-doped via a charge transfer between graphene layers and SiC. For SLG and BLG, the total density of charge is about 10²³ cm⁻² as reported by Ohta and co-workers [44].

Figure 1(a) (top) shows a constant current STM image of a WSe₂ flake transferred on such a graphitized SiC substrate. Only a small part of the flake is shown here, although its overall size is several tens of micrometers (see figure S1 in the supplementary information (SI)). The edge of the flake is also present in figure 1(a) (pointed by the green arrow), delimiting the boundary between the WSe₂ flake and the uncovered graphene region.
As deduced from STM height measurements (see figure 1(a) bottom), the WSe$_2$ flake consists of three layers (3L), and is homogeneous on micrometer distances (see figure S1). We observe that the 3L-WSe$_2$ flake covers several steps of the substrate: the flake adheres well and conforms to the Gr/SiC terraces. We also draw the same conclusion by analyzing the large scale STM image of figure S1(b) in the SI. Among different steps seen on the WSe$_2$-covered area of figure 1(a), the one separating the regions labelled A and B is of particular interest. Indeed, after completing the STS measurements on the TMD flake, the WSe$_2$ layer could be locally removed with the STM tip, exposing the underlying graphene film. We could thus identify directly by STM the nature of the substrate terraces (see section B of the SI), which is SLG for region A and BLG for region B, as illustrated in figure 1(b). This allows us to investigate the impact of these two graphene phases on the electronic properties of the 3L-WSe$_2$ flake. Interestingly, such an STM/STS study can be performed with the same tip, due to the fact that A and B regions are very close to each other.

The electronic properties of the 3L-WSe$_2$ regions residing on SLG and BLG are probed by performing spectroscopic measurements (dI/dV(V) spectra) at various points on the terraces A and B. Because individual curves taken on each region are identical, averaged spectra (blue and red curves in figure 1(c)), obtained on A: 3L-WSe$_2$/SLG and B: 3L-WSe$_2$/BLG terraces respectively are meaningful with a higher signal-to-noise ratio. Here, the blue curve is shifted vertically with respect to the red one for clarity. As can be seen, these spectra are very similar in shape, with a large bias region with a vanishing conductance corresponding to the electronic bandgap of the WSe$_2$ film.

For both curves, the Fermi level, $E_F$ (located at zero bias on the dI/dV spectra), is closer to the conduction band minimum (CBM) than to the valence band maximum (VBM). This indicates a low n-type doping for the 3L-WSe$_2$ flake disregarding the underlying substrates, either SLG or BLG. This is different from the strong p-type doping reported for WSe$_2$ samples of different origin (studied in [32]). For 3L-WSe$_2$/BLG, the VBM and CBM stay at $\sim$−1.0 V and $\sim$−0.5 V from $E_F$, respectively, as highlighted by the dashed lines in figure 1(c) and figure S3. The n-doping together with a gap of roughly 1.5 eV estimated from the positions of VBM and CBM agree well with the results obtained by Bradley et al for 3L-MoSe$_2$ flakes grown on a BLG substrate [45]. This is reasonable since similar gaps have been measured for single-layer WSe$_2$ and MoSe$_2$ samples prepared on BLG substrates [20, 45, 46]. In addition to similar bandgaps and n-type doping, both blue and red curves also exhibit a clear bump (pointed by arrows in figure 1(c)). The only striking difference between the two spectra shown in figure 1(c) is that one curve is bias-shifted from another: for instance the bump in the occupied states stays at about $−1.66$ V and $−1.53$ V for the blue and the red curves, respectively.

![Figure 1](image-url)

**Figure 1.** STM/STS results obtained on a 3L-WSe$_2$ flake transferred on a graphitized SiC(0001) substrate: (a) Top: a constant current STM image of a small part of the flake. Image size: 240 × 65 nm$^2$, sample bias: −2.0 V, tunneling current: 0.14 nA. Bottom: a height profile taken along the pink line drawn in the STM image. The numbers indicate the step height in nanometre. Green arrows (in top and bottom panels) indicate the position of the edge of the flake: bare Gr/SiC is found on the right part of this edge. From the measured edge height (1.9 nm), we deduce that the flake consists of three layers (3L). This thickness is homogenous, but various terraces of the Gr/SiC substrate show up below the flake. Terraces labelled A and B are identified as WSe$_2$ on single-layer graphene (SLG) and bilayer graphene (BLG) respectively, as detailed in section B of the SI. (b) A schematic view of the vertical stacking corresponding to terraces A and B sketched in (a). (c) dI/dV(V) spectrum obtained by averaging individual spectra recorded on the WSe$_2$/SLG (A: blue curve) and on the WSe$_2$/BLG (B: red curve) terraces. Setpoint parameters: sample bias = −2.0 V, tunneling current = 0.14 nA. The blue curve is shifted vertically for clarity. To estimate the voltage shift between the two spectra, an additional curve drawn with open orange circles is used. This curve is obtained by resizing (signal-to-noise ratio). Here, the blue curve is shifted vertically with respect to the red one for clarity. As can be seen, these spectra are very similar in shape, with a large bias region with a vanishing conductance corresponding to the electronic bandgap of the WSe$_2$ film.
A precise determination of the shift between the two spectra can be achieved via an alignment procedure: by multiplying the dI/dV signal measured on 3L-WSe2/SLG by 0.5 and then by shifting it by a value of +110 mV, we obtained a new ‘shifted’ curve (represented as open orange circles in figure 1(c)), which overlaps the red curve quite well. A satisfactory alignment can be obtained by varying the shift by ±20 mV. Thus, for the studied region, the spectrum obtained on 3L-WSe2/BLG is rigidly shifted by +110 ± 20 mV with respect to the one measured on 3L-WSe2/SLG. This shift does not originate from an STM-related phenomenon, like a possible tip-induced band-bending, resulting from a difference in the tip-sample distance between BLG and SLG covered areas, as discussed in section D of the SI. Moreover, this result is not specific to this spot of the flake, since it is also found in other places of the sample (discussed in section C of the SI).

Now, due to the finite thickness (2 nm) of the 3L-WSe2 sample under study, the measured shift may slightly differ from the one at the WSe2/graphene interface owing to a residual band-bending perpendicular to the interface. Therefore, similar alignments on thinner flakes would allow us to better probe the effect induced by the graphene substrates. To check this point out, and also to verify that the results shown in figure 1(c) hold for other vdW semiconductor-graphene heterostructures, we have investigated single-layer (1L) MoSe2 flakes grown by MBE on Gr/SiC (0001) substrates (see Methods).

Figure 2(a) is a typical STM image, where a continuous 1L-MoSe2 island with sizes ranging between 10–100 nm lays on the graphitized SiC substrate. From the profile shown in the inset of the same panel, the edge of the MoSe2 flake is 8 Å high. Since the STM tip simultaneously records the corrugation and the electronic properties of the surface, the apparent height of the edge slightly differs from the expected interlayer spacing (6.7 Å) of a bulk MoSe2 crystal.

A derivative (dz/dx) of the STM image displayed in figure 2(a) reveals periodic features at the nanometer scale on the bare graphene terraces (see figure 2(b)). As reported in previous STM works [33, 47, 48], these features arise from the buffer layer and are detected by STM as periodic modulations on SLG and BLG. The corrugation of these features decreases with the increasing thickness of the few-layer graphene films [48]. Since single-layer and bilayer graphene are the dominant phases on our sample, we conclude that the bottom and the top graphene terraces are SLG and BLG, respectively. This is confirmed by atomically resolved STM images obtained on these two terraces (see insets in figure 2(b)), which show the usual honeycomb-like (triangular-like) contrast for SLG (BLG) [33]. Thus, the small part of the MoSe2 flake shown in figure 2(c) covers at the same time these two terraces like the WSe2 sample presented in figure 1.

The spectroscopic characterization of the 1L-MoSe2 flake shown in figure 2 is summarized in figure 3. We have collected a series of STS spectra at 128 points along a 15 nm long line crossing the step separating the two MoSe2/BLG and MoSe2/SLG regions (see arrow in figure 2(c)). The resulting color-coded dI/dV(x,V) map is given in figure 3(a). A z(x) height profile (a white solid curve) measured along the same line is also added in order to identify the position of the BLG/SLG step.

Figure 3(a) shows that the spectra measured on monolayer MoSe2 on either side of the step are rather
similar, with band onsets in the same energy range and a Fermi level close to the CBM, as for 3L-WSe2 sample. In addition, no in-gap states are present all along the line, and in particular at the step position. The most salient result shown here is the smooth shift (in the 100 mV range over 2–3 nm) of the band onsets towards negative bias when going from MoSe2/BLG to MoSe2/SLG.

To be more quantitative, we refer to figure 3(b) showing the spatially averaged $\text{d}I/\text{d}V(V)$ spectra obtained on the two different regions, derived from the data of the panel (a) of the same figure. The red and blue curves correspond to the MoSe2/BLG and MoSe2/SLG phases respectively. The dominant feature in the valence band for each spectrum is a pronounced $\text{d}I/\text{d}V$ peak below $-2.0$ V (this peak is also indicated on figure 3(a) by a horizontal arrow). From the $\text{d}I/\text{d}V(V)$ spectra, we find that on the MoSe2/BLG region, this peak is located at $-2.07 \pm 0.01$ V (highlighted by the arrow in figure 3(b)), a value close to those reported by other groups [20, 38, 45]. This structure (hereafter called $\Gamma$ peak) corresponds to a valence band feature at the $\Gamma$ point but not to the VBM, which is located at higher energy at the K-point of the Brillouin zone [20]. Owing to their large in-plane vector and small out of plane component, electronic states at the VBM provide a very weak signal in STS spectra [20, 45] and thus the VBM is hardly seen in the color map presented in figure 3(a).

From figure 3(b), we find that the $\Gamma$ peak for MoSe2/SLG is located at $-2.20 \pm 0.01$ V, i.e. 130 mV below the $\Gamma$ peak found for MoSe2/BLG. Applying the same procedure as described for the spectra obtained on 3L-WSe2 in figure 1(c), we can construct a shifted $\text{d}I/\text{d}V(V)$ curve (open orange circles in figure 3(b)) by resizing the MoSe2/SLG curve: the amplitude of the signal is multiplied by 1.4, and the curve is bias-shifted by $+130$ mV. These values are chosen in order to align the $\Gamma$ peak of the orange and the red curves (from the uncertainty in the position of this peak the shift can be varied over $\pm 20$ mV). From this alignment procedure, it appears that all the other features of the orange and red curves in figure 3(b) are also fairly well aligned. The onsets of the conduction band at positive bias almost coincide. Moreover, the inset of figure 3(b) shows that up to 0.5 V above the $\Gamma$ peak (black arrow), the $\text{d}I/\text{d}V$ signal, which arises from the top of the valence band [20], behaves similarly for the orange and red curves. Although the use of a large tunneling resistance in this measurement hinders an accurate determination of the VBM position, the data of figure 3 indicate a global shift by $+130 \pm 20$ mV of the band structure of MoSe2 between SLG and BLG substrates. The section E

Table 1. Summary of the different values/numbers (scaling factors, measured band shifts) given in the main text and in the SI for the investigated junctions. The number of spectra considered for each phase (TMD/SLG or TMD/BLG) is also indicated.

| Sample   | Figure | Number of spectra per phase | Scaling factor | Bias-shifts $\pm 20$ mV |
|----------|--------|------------------------------|----------------|--------------------------|
| 3L-WSe2  | 1      | 4                            | $\times 0.5$  | 110 mV                  |
| 3L-WSe2  | S3     | 20                           | $\times 3$    | 110 mV                  |
| 1L-MoSe2 | 3      | 40                           | $\times 1.4$  | 130 mV                  |
| 1L-MoSe2 | S6     | 10                           | $\times 2.2$  | 135 mV                  |
of the SL shows data obtained on another 1L-MoSe\textsubscript{2} flake where essentially the same value of the band displacement (135 mV) is observed. Since this shift of the band structures takes place within about 2.5 nm (figure 3(a)), the voltage drop of 130 mV corresponds to a built-in electric field of \(\sim 5 \times 10^7\) V m\(^{-1}\), which is a typical value for boundaries existing in similar systems [38, 39].

To sum up our main results, we report a systematic bias-shift by 110–135 mV between the spectra measured on TMD/BLG and TMD/SLG (see table 1). This value is almost independent of the chemical composition (MoSe\textsubscript{2} and WSe\textsubscript{2}) or of the thickness (1L and 3L) of the TMD materials. In consequence, this effect should also exist in vertical stacks of SLG/BLG and other few-layer TMD semiconductors as well.

In order to interpret the observed bias-shifts, we consider this system as a metal-semiconductor (MS) interface between 2D materials bonded by van der Waals interaction. Since the graphene layers are heavily doped, they can actually be treated as 2D metallic electrodes, and we are thus dealing with two different MS interfaces: SLG/TMD and BLG/TMD. As shown above, the band structures of 1L-MoSe\textsubscript{2} and 3L-WSe\textsubscript{2} both move in the same direction and by alike values when going from one interface to another. The similar shifts were observed for two semiconducting TMDs which have different electronic structures in details: their gap size differs from each other, their VBM are located at dissimilar points in the reciprocal space [21, 38] and their electronic affinities and ionisation potentials are presumably unequal. It is thus reasonable to ascribe the (common) value of the shift summarized in table 1 to a difference in the intrinsic properties of the two supporting graphene phases.

In the context of MS junctions, the most obvious quantity to be considered is the metal work function, \(\phi_M\), as widely discussed in the literature [15, 28–30]. Indeed, in the basic Schottky-Mott model for MS junctions, the energy difference between the CBM of the semiconductor and the Fermi level of the metal or the Schottky barrier height (SBH) at the interface is given by \(\mathrm{SBH} = \phi_M - \chi\), where \(\chi\) is the electron affinity of the semiconductor [15, 28–30]. Thus, for a given semiconductor the position of the CBM and of the VBM with respect to the Fermi level at the interface should vary linearly with \(\phi_M\). Previous experiments have shown that the work function (\(\phi_{\text{BLG}}\)) of clean BLG on SiC(0001) is larger than the one of SLG (\(\phi_{\text{SLG}}\)) on the same substrate [24–27]. Using this result, the band offsets at SLG/TMD and BLG/TMD interfaces expected from the Schottky-Mott model are schematically depicted in figure 4. The shift of the valence and conduction bands of the TMD with respect to the Fermi level between SLG and BLG substrates is in the same direction as in our measurements. Additionally, from this model, the amplitude of the shift should be \(\phi_{\text{BLG}} - \phi_{\text{SLG}}\). By using Kelvin probe microscopy, Filletier and co-workers [24] found that \(\phi_{\text{BLG}} - \phi_{\text{SLG}} = 135 \pm 9\) meV. Consistent values were reported by Hibino et al [27] (100 \pm 50 meV) and Renault et al [25] (60 \pm 60 meV) using photoemission. The value reported by Filletier et al [24] is pretty close to the one we have experimentally found for the bias shift, i.e. for the increase of the SBH, which is 120 \pm 20 meV. This quantitative agreement clearly indicates the absence of the Fermi level pinning at the TMD/graphene interface, where the S parameter of the junction (\(S = d\text{(SBH)/d}\phi_M\)) is thus close to 1 [15, 29]. It also suggests that the Schottky-Mott rule may
be valid for these MS junctions between 2D materials (see the section F of the SI for further comments). Although we cannot exclude the presence of an interface dipole [28], it should be identical for TMD/SLG and TMD/BLG to preserve the linear dependence of the SBH on $\phi_M$ [30].

On the theoretical side, Liu and co-workers [28] have recently predicted that the Fermi level pinning is weak at van der Waals (vdW) semiconducting TMD-2D metal interfaces and, accordingly, that the SBH essentially follows the Schottky-Mott model with $S \approx 1$. According to these authors, this interesting behaviour results from the absence of metal-induced gap states (MIGS) and/or defect-states that could pin the Fermi level in the TMD gap. The lack of MIGS is ascribed to the weak interaction in vDW junctions [28]. Within the spots we have investigated in this work, we indeed found no evidence for electronic states at (or close to) the Fermi level inside the TMD gap (see spectra in figures 1(c) and 2(c) and in the SI). Our experimental findings obtained on vdW-based MS junctions are thus in excellent agreement with the theoretical prediction discussed in [28].

Finally, we emphasize that the weak Fermi level pinning at graphene/TMD interfaces is unique to vertical stacks of vdW materials, because as reviewed by Allain et al [31], deposited metallic electrodes, like Co, Ni, W etc show the opposite behaviour. The metal-TMD interaction leads to a strong Fermi level pinning with the S parameter much smaller than 1 for these junctions.

4. Conclusion

We have investigated the impact of graphene substrates (single-layer and bilayer graphene on SiC(0001)) with different work functions on the electronic properties of thin TMD films (WSe$_2$ and MoSe$_2$) by scanning tunneling microscopy and spectroscopy (STM/STS) in ultra-high vacuum. A rigid shift of about 120 mV between the STS spectra obtained on flakes residing on SLG and BLG substrates has been observed for all the studied samples regardless of their chemical composition and their thickness (one or three layers). Furthermore, this shift, corresponding to the band offsets of the TMD materials, is almost equal to the difference in the work function of SLG and BLG substrates. This gives strong evidence for a very weak Fermi level pinning at graphene-TMD interfaces, in line with the Schottky-Mott model, as predicted for this type of van der Waals heterostructures.

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