Impact of mid-gap states on transport in single-crystal Graphene-MoS₂ heterojunctions integrated into a multi-FET architecture

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Abstract

We demonstrate a graphene-MoS₂ architecture integrating multiple field-effect transistors and we independently probe and correlate the conducting properties of van der Waals coupled graphene-MoS₂ contacts with the ones of the MoS₂ channels. Devices are fabricated starting from high-quality single-crystal monolayers grown by chemical vapor deposition and characterized by scanning Raman and photoluminescence spectroscopies. Transconductance curves of MoS₂ are compared with the current-voltage characteristics of graphene contact stripes, revealing a significant suppression of transport on the n-side of the transconductance curve. Based on ab-initio modeling, the effect is understood in terms of trapping by sulfur vacancies, which counter-intuitively depends on the field-effect, even though the graphene contact layer is positioned between the backgate and the MoS₂ channel.

Keywords

graphene, MoS₂, heterostructure, field-effect, single-crystal

Letter

Van der Waals (vdW) heterostructures, formed when two or more atomically-thin crystals are bonded by vdW interaction, are intriguing architectures, enabled by the discovery of two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides (TMDs). Within this family, peculiar junctions can be obtained when graphene is used as a contact material for a TMD monolayer. While the interface between a TMD and a conventional, bulk metallic electrode tends to display Schottky behavior due to intrinsic and extrinsic Fermi pinning phenomena, vdW graphene-TMD junctions yield well-behaved linear transport characteristics. This contacting approach has been successful in improving TMD-based devices. Nev-
ertheless, the exact physics behind graphene-TMD vdW junctions is still debated and difficult to probe in a direct way. In particular, devices typically include only two contacts, which makes effects on the transport characteristics due to the interface not easy to distinguish from those due to the resistivity of the two-dimensional materials, since typically only the global conductance of the device can be measured.

Charge transfer phenomena, strain, and charge trapping in defects might also play an important role. Furthermore, in the case of field-effect devices, the low density of states in the vicinity of the Dirac point leads to weak screening properties despite the metallic nature of graphene. This implies that a non-trivial response to field effect can be observed, and exploited in novel device concepts. Gating on graphene-MoS$_2$ heterostructures has been widely investigated from a numerical and experimental point of view, and in different stacking configurations. Indeed, the reciprocal electrostatic screening of the junction materials can remarkably affect the contact resistance, and it was shown theoretically that MoS$_2$ can screen the field effect on graphene, or not, depending on the order of the specific stacking sequence. Nevertheless, to the best of our knowledge, direct experimental evidence of how the formation of vdW interfaces leads to changes in the transport properties of the individual materials involved in field-effect transistor (FET) devices is still missing.

The progress of large-scale chemical vapor deposition (CVD) techniques gives the opportunity to investigate vdW interfaces from a different angle. High-quality and large-scale monocrystalline flakes of graphene and TMDs can be reproducibly grown. When this technique is associated with a patterning of the seed points, predictable flake arrays of chosen sizes can be achieved, opening to a promising pathway to the fabrication of multiple parallel devices combining different 2D materials. In this Letter, we take advantage of this opportunity to demonstrate a novel graphene-dichalcogenide architecture where a monocrystalline MoS$_2$ channel is contacted by a large number of monocrystalline graphene stripes, each of them crossing the whole MoS$_2$ channel as schematized in Fig. 1. Each stripe can thus act as ohmic contact for a MoS$_2$ backgated FET (see cross-section AB in Fig. 1), and be simultaneously contacted at its terminations to implement an additional MoS$_2$-covered graphene FET (cross-section CD in Fig. 1). This structure can so act as a MoS$_2$ FET and as a set of graphene FETs at the same time, which will be referred to as a multi-FET in the following. Such unique arrangement allows a first independent study of the conducting properties to be performed for the different components of graphene-MoS$_2$ systems, highlighting a suppression of the electron-side transconductance in MoS$_2$-covered graphene, in coincidence with the conducting threshold of free MoS$_2$ in the main device channel. This behavior is apparently at odds with recent predictions for defect-free MoS$_2$, nonetheless it can be understood in terms of a gate-driven trapping by sulfur va-

Figure 1: Multi-FET device architecture. (a) Monocrystalline contact stripes obtained by patterning a periodic array of graphene CVD flakes (scale bar is 100 µm). (b) Monocrystalline CVD MoS$_2$ flakes before transfer onto the SiO$_2$/Si substrate (scale bar is 50 µm). (c) Optical picture of one of the studied devices implementing a multiple FET structure, as visible in the cross-section sketches: graphene multi-contact MoS$_2$ FET (AB section) and MoS$_2$-covered graphene FET (CD section).
cancies which further highlights the non-trivial weak screening properties of graphene.

The multi-FET fabrication starts from a square array of \( \approx 150 \mu m \)-wide single-crystal monolayer graphene flakes, with a spacing of 200 \( \mu m \). Arrays are grown on Cu foil via CVD\(^{20}\) and then transferred on a p++ Si substrate covered by 300 nm thermal SiO\(_2\) following the procedure described in Ref. 22. Each flake is patterned into a set of 5 \( \mu m \)-wide and 5 \( \mu m \)-spaced stripes via electron-beam lithography followed by reactive ion-etching, leading to the structures visible in Fig. 1c. Single-crystal MoS\(_2\) monolayer flakes with an average size of \( \approx 50 \mu m \) were grown via CVD following Ref. 27 and 28 (see Fig. 1b). Given the chosen spacing between the stripes, the process typically yields various devices with 4 – 5 contacts and, since the flakes are triangular, with an uneven coverage of the graphene stripes. The transfer process employed for MoS\(_2\) is very similar to the one for graphene except for the delamination step, which was obtained by immersing the sample in a 1 M solution of NaOH rather than by an electrochemical method.\(^{22}\) After the transfer, excess MoS\(_2\) flakes were removed by a further dry etching step and, finally, metallic Cr/Au (10/50 nm) electrodes were defined by electron-beam lithography and thermal evaporation. Each fabrication process yields various devices in parallel, one of them visible in Fig. 1f. Further details about fabrication are reported in the experimental methods in the Supporting Information (Fig. S1a shows a schematic of the fabrication procedure).

Both the patterning procedures and the formation of vdW interfaces can significantly perturb the properties of the 2D materials. For this reason, photoluminescence (PL) and Raman spectroscopy were employed to characterize the 2D crystals at relevant device processing steps. In Fig. 2a-c, we report Raman spectra of a typical transferred MoS\(_2\) flake and analyze the influence of the graphene contact stripes. The characteristic \( A_{1G} \) and \( E_{2G} \) modes visible in panel (a) exhibit a strong dependence on thickness\(^{33}\) and their separation \( \Delta \omega \approx 19 \) cm\(^{-1}\) is in good agreement with the expected monolayer nature of the MoS\(_2\) flake. Raman data contain also information on the local doping and strain, which can be analyzed based on the correlation plot in Fig. 2b, where the position of the \( A_{1G} \) peak is plotted against the one of \( E_{2G} \).\(^{29}\) Mean Raman shifts of the \( E_{2G} \) and \( A_{1G} \) peaks in graphene-free regions are 384.5 ± 0.3 cm\(^{-1}\) and 403.3 ± 0.4 cm\(^{-1}\), respectively. These values are quite close to the neutrality point, located at the intersection between zero strain and zero doping line (\( E_{2G} = 384.6 \pm 0.2 \) cm\(^{-1}\) and \( A_{1G} = 402.7 \pm 0.2 \) cm\(^{-1}\)).\(^{29}\) Interestingly, Raman shifts from regions where MoS\(_2\) overlaps graphene (\( E_{2G} = 383.4 \pm 0.5 \) cm\(^{-1}\) and \( A_{1G} = 404.3 \pm 0.3 \) cm\(^{-1}\)) indicate a variation in tensile strain distribution of \( \approx 0.10 \) – 0.35% and a sizable electron reduction of \( (3.0 \pm 1.8) \times 10^{12} \) cm\(^{-2}\). Thanks to the sensitivity of the \( A_{1G} \) peak on doping,\(^{34}\) the spatial doping modulation of MoS\(_2\) due to graphene can be directly appreciated in the map of the \( A_{1G} \) position in Fig. 2f. The map is shown in overlay to an optical picture of the flake, to highlight the good correlation between the map patterns and the position of the graphene stripes. Consistent evidences are obtained from graphene Raman data shown in Fig. 2h-f. In panel (d), graphene spectra in the presence/absence of MoS\(_2\) are compared. Both curves show a single sharp Lorentzian-shaped 2D peak, which is a typical signature of monolayer graphene,\(^{33}\) and no D peak, which indicates a negligible density of defects.\(^{34}\) The absence of defects was confirmed for all the fabrication steps (see Supporting Information Fig. S2). We also note that when graphene is covered in MoS\(_2\) (orange curve), a strong baseline appears below the Raman peaks due to the MoS\(_2\) PL signal. As in the case of MoS\(_2\), strain and doping profiles can be derived from the Raman data,\(^{30}\) based on the correlation plot of the 2D and G modes reported in Fig. 2b, see Supporting Information for additional correlation plots (Fig. S1c-f). The positions of the G and 2D peaks in regions free from MoS\(_2\) are 1582.7 ± 0.9 cm\(^{-1}\) and 2676.2 ± 2.2 cm\(^{-1}\), respectively, corresponding to a \( p \)-type doping. Differently, Raman data collected in MoS\(_2\)-covered regions (1585.4 ± 1.5 cm\(^{-1}\) and 2685.8 ± 3.7 cm\(^{-1}\) for the G and 2D peaks, respectively) fall on the strain line, thus indicating a neutralization
Figure 2: Optical characterization of the MoS₂-graphene structures. (a) MoS₂ Raman spectra after transfer on top of the graphene stripes: both spectra from MoS₂ on top of graphene (orange) and graphene-free MoS₂ (blue) are reported. (b) Correlation plot of the position of A₁G as a function of the position of E₂G. Zero strain and zero doping line are taken from Ref. 29 (514.5 nm laser excitation). (c) Map of the position of A₁G. (d) Raman spectra of graphene after the MoS₂ transfer: both spectra in the presence (orange) and absence (green) of the MoS₂ overlayer are reported. (e) Correlation plot of the position of 2D peak as a function of the position of G peak. Zero strain and zero doping line are taken from Ref. 30 (514.5 nm laser excitation) (f) Map of the position of 2D peak. (g) PL spectra of MoS₂ both in a region where it overlaps graphene (orange) and in a graphene-free region (blue). Gaussian fits of A and B excitons are shown in dashed and dot-dashed lines respectively. (h) Map of the position-dependent quenching of the A exciton signal. (i) Map of the position-dependent A exciton broadening. All maps are shown in overlay to an optical image of the analyzed flake, scalebars in the panels correspond to 10 µm.
of graphene. The variation of mean peaks positions corresponds to an electron increase of \((2.3 \pm 1.5) \times 10^{12} \text{ cm}^{-2}\) and to a variation of strain nature from compressive to tensile. The spatial modulation of the doping can be seen from the 2D peak position map in panel (f), showing a good correlation with the position of the MoS\(_2\) flake. A modified strain is also observed, turning from slightly tensile to compressive \(\approx 0.10 - 0.30\%\). We note that the doping and strain trends observed where MoS\(_2\) and graphene overlap are opposite and thus consistent. We further highlight that while Raman data clearly indicate an electron transfer from MoS\(_2\) to graphene, absolute equilibrium carrier densities are not obvious to be determined, due to the presence of photo-excited carriers during the Raman measurements. The formation of the heterojunction can be further investigated based on the PL spectra of MoS\(_2\), which are reported in Fig. 2g. Three main peaks are highlighted by Gaussian deconvolution. These peaks are attributed to the A exciton (1.81 eV), the B exciton (1.94 eV) and the trion (1.71 eV) \[35,36\] We observe that the presence of graphene modifies the MoS\(_2\) response and the signal of the A exciton is quenched when MoS\(_2\) is coupled to graphene (orange curve) with respect to stand-alone MoS\(_2\) (blue curve): indeed, a lowering of the A intensity by \(\approx 30\%\) and a lineshape broadening from \(\approx 66\) meV to \(\approx 96\) meV is retrieved. The spatial modulation of the effect can be directly appreciated from the maps of the intensity and width of the A exciton in Fig. 2h and Fig. 2i, respectively. Additional spectroscopic data are reported in the Supporting Information (S5-S9).

The graphene stripes form ohmic contacts to the MoS\(_2\) channel and lead, at room temperature and in vacuum conditions \((P < 10^{-5}\) mbar\), to highly linear two-wire IV curves over the \(\pm 2\) V range. In Fig. 3a, we report the \(I_{SD} vs V_{SD}\) characteristics of a representative MoS\(_2\) FETs, measured as a function of the gate voltage \((V_G)\) in the \(0 - 80\) V range. The transfer characteristic in Fig. 3b indicates a positive threshold voltage, with a sizable clockwise hysteresis, as frequently reported in literature for FETs based on 2D materials and nanowires,\[37-41\] as well as in Kelvin probe microscopy experiments.\[42\] The effect is generally ascribed to the slow dynamics of trap states leading to a time-dependent screening
Figure 4: Effect of the MoS$_2$ overlayer on electron transport in the graphene contact stripes. (a-b) Optical images of the two devices used to estimate the effect of different MoS$_2$ coverage levels on conduction in the graphene stripes. Used contacts are highlighted by colored dots. (c-g) Transfer characteristics of the graphene stripes for different MoS$_2$ coverages ranging from 0% to 79%. The curve colors match the ones used to highlight the contacts in panels (a) and (b): red 48%, blue 55%, yellow 69%, purple 79%; the black curve corresponds to a reference MoS$_2$-free graphene stripe (device image not shown).

The method also neglects the effect of contact resistances, which may lead to a mobility underestimation but are not expected to have a significant effect in the explored transport regime, based on preliminary four-wire measurement data.

Our multi-FET devices were specifically designed for comparing the MoS$_2$ transport characteristics with the electron configuration in the graphene stripes, which play here the dual role of the contact in the MoS$_2$ FET and of the channel in MoS$_2$-covered graphene FETs. The IVs of all our graphene stripes are found to be highly linear (data not shown) and in Fig. 4 we report the transfer characteristic of various graphene FETs as a function of the $V_G$, from which we obtain a mobility $\approx 4085 \text{ cm}^2/\text{Vs}$. In the plot sequence (c-g), we compare the conductivity of stripes characterized by a different MoS$_2$ coverage: conductivity is calculated from the total resistance using the geometrical form factor of the stripe and contact resistances are estimated by comparing the $p$-side of the gate sweeps; MoS$_2$ coverage is quantified

Figure 3: (a) Optical image of the graphene stripes. (b) Schematics of the field effect of the gate. Trap states may have several origins, including defects at the SiO$_2$ substrate interface, adsorbates, or MoS$_2$ point defects. In our devices, possible sources of traps include interfaces between MoS$_2$, graphene and SiO$_2$ (see AFM data in the Supporting Information S-10) as also S vacancies in MoS$_2$, which are known to occur in quite large densities (typically few $10^{13} \text{ cm}^{-2}$) in CVD flakes. The field-effect mobility of MoS$_2$ carrier can be estimated from the transfer characteristic according to

$$\mu = \frac{dG}{dV_G} \frac{L^2}{C_G},$$

where $C_G$ is the capacitance and the MoS$_2$ trapezoid channel sketched in the inset of Fig. 3 is approximated as a rectangle with a length $L = 5.5 \pm 0.3 \mu\text{m}$ and width $W = 19.5 \pm 0.5 \mu\text{m}$. Considering both curves in the hysteresis loop, we extract two mobility values $\approx 5.3 \text{ cm}^2/\text{Vs}$ and $\approx 8.6 \text{ cm}^2/\text{Vs}$. Similar analysis on different FETs yielded field-effect mobilities in the range $5.3 - 6.6 \text{ cm}^2/\text{Vs}$. Given that gate hysteresis generally indicates that part of the gate-induced carriers end in charge traps, field-effect measurements are known to overestimate the carrier density induced in the channel and to underestimate mobility. Both the mobility values above should thus be considered as a lower bound to the true room temperature electron mobility in the specific MoS$_2$ flake. The method also neglects the effect of contact resistances, which may lead to a mobility underestimation but are not expected to have a significant effect in the explored transport regime, based on preliminary four-wire measurement data.
from the ratio between the area of the MoS$_2$-graphene and the graphene regions, see optical pictures in Fig. 4a-b. Coverage goes from 0\% (MoS$_2$-free graphene in panel (c)) to 79\% (panel (g)). A clear trend is observed in the transfer characteristics: curves go from a conventional ambipolar behavior in panel (c) to a limit of strongly quenched n-type conduction for the largest coverage in panel (g). The observation of a quenching of field effect in graphene-TMD heterostructures has been reported in the literature, for instance in WS$_2$-graphene heterostructures and in graphene functionalized with different materials, such as TiO$_2$ or organic molecules as well\textsuperscript{13,14,46–48}. On the other hand, the observed behavior is somewhat puzzling since, ideally, MoS$_2$ should not affect carrier density in graphene when positioned on top of back-gated graphene due to the reciprocal screening in the vdW heterostructure\textsuperscript{13}

Our analysis allows for identifying the origin of this apparent discrepancy as due to vacancies in TMDs\textsuperscript{13,14} which are also likely a main cause of the hysteretic behavior reported in Fig. 3. Using Density Functional Theory (DFT)\textsuperscript{53} we made an ab-initio analysis of the electronic states of graphene-MoS$_2$\textsuperscript{54} in the presence of sulfur vacancies: these have an energy that falls in the gap\textsuperscript{55} of MoS$_2$ and are located at a distance of few Angstroms from graphene, so their effect is hard to evaluate without a first-principles approach (see Methods and Supporting Information for further details). Numerical calculations were performed using a density of S-vacancies of $\rho_v \approx 7.5 \times 10^{13}$ cm$^{-2}$. In Fig. 5 we report the electronic band structure and projected density of states (DOS) of the graphene-MoS$_2$ heterostructure for $V_G = 0$: as visible in the plot, the Fermi energy of the system lays in the proximity of MoS$_2$ mid-gap states generated by the S-vacancies. This suggests that such states may influence the mobile carrier density induced in the graphene layer by the gate when $V_G \neq 0$. This is confirmed by calculations performed at different values of $V_G$, where the distribution of the resulting excess of carrier density is evaluated by means of the topological analysis of the electron density, using the Bader procedure\textsuperscript{19,20,56,57}. As shown in Fig. 5b, even if MoS$_2$ is placed on top of graphene, it affects the carrier density induced by the gate in the graphene layer. In particular, the n-side of the field-effect response is reduced by $\approx 50\%$; this, combined with the likely increased scattering caused by the large DOS close to the Fermi energy, clearly reproduces the behavior reported in Fig. 4. In Fig. 5c-d, the atomistic structure and the model of the typical setup for a field-effect measurement are shown. The charge density isosurfaces, together with the planar averaged carrier charge density, give a pictorial view of the different behavior with negative and positive backgate voltages. We point out that our results do not contradict, but rather complement, the conclusion drawn in recent literature\textsuperscript{13} calculations also show that no charge transfer is obtained in the case of defect-free MoS$_2$ since in that limit the TMD cannot support any electron state in the relevant energy range (see Supporting Information Fig. S8). Nonetheless, it is interesting to highlight that, in the presence of vacancies, a TMD overlayer can indeed have a remarkable impact on the backgate response of these vdW heterostructures and of devices based on them, extending the range of non-trivial consequences of the weak screening properties of graphene.

In conclusion, we have demonstrated a graphene-MoS$_2$ architecture integrating multiple graphene-contacted MoS$_2$ FETs and MoS$_2$-covered graphene FETs and used it to correlate the field-effect characteristics of a MoS$_2$ monolayer with the conducting properties of graphene used to contact it. Such a study cannot be performed in a conventional FET structure since the individual resistive contributions cannot be discriminated in any obvious and direct way. Our results show that MoS$_2$ can affect the field-effect conduction of a back-gated graphene monolayer, even when placed on top of the vdW stack, and the suppression of conduction in the graphene stripes is observed over a gate voltage range which is consistent with the conduction threshold of the MoS$_2$ channel. This behavior is explained in terms of a filling of sulfur vacancies in the MoS$_2$, as supported by ab-initio calculations.

**Methods.** Further details on the fabrication
Figure 5: Field-effect response in the presence of S-vacancies. The impact of sulfur vacancies was simulated by removing one S atom from a MoS\textsubscript{2} supercell (density of S-vacancies of $\rho_v \approx 7.5 \times 10^{13} \text{cm}^{-2}$). (a) Supercell band structure and projected density of states (DOS) of the Graphene-MoS\textsubscript{2} interface; the red dashed line indicates the Fermi energy $E_F$. In the DOS plot, pristine graphene is indicated with a continuous line and the S-vacancy appears as a peak close to the Dirac point. (b) Field-effect induced charge distribution as a function of gate voltage $V_G$, evaluated as the difference between the gated ($V_G \neq 0$) and ungated case ($V_G = 0$); the topological analysis of the electron density was done by means of the Bader procedure.\textsuperscript{49–52} The solid (dashed) red line indicates the excess holes on the graphene (MoS\textsubscript{2}) monolayer, while the solid (dashed) blue line indicates the excess electrons. In order to mimic the experimental values, the values of $V_G$ are rescaled considering that there is a 300 nm thick layer of SiO\textsubscript{2} between the metal gate and the Graphene-Mo\textsubscript{2} interface. (c-d) Side view of the gated Graphene-MoS\textsubscript{2} interface. In the two panels, the charge isosurface for $V_G < 0$ (left) and $V_G > 0$ (right) is evaluated as the difference between the charge densities for the gated and ungated limit; on the two sides, the averaged surface charge density is shown considering S-vacancies with doping $n \approx -1.2 \times 10^{13} \text{cm}^{-2}$ which correspond to $V_G \approx +45 \text{ V}$ in panel b. The location of the S-vacancy is marked by the green ball.
are reported in the Supporting Information (S3-S4). The properties of graphene and MoS$_2$ were monitored by Raman and photoluminescence spectroscopy, using a Renishaw InVia spectrometer equipped with a 532 nm laser. Laser power was $\approx 1$ mW and the typical acquisition time was $4$ s.\textsuperscript{58} Transport measurements were performed in a vacuum chamber using source-measure units K4200 and K2614B and a Femto DDPCA-300 current preamplifier. We investigated how field-effect doping affects the electronic structure carrying out DFT calculations by using the QUANTUM ESPRESSO (QE).\textsuperscript{59–63} To obtain information on the charge transfer between the two moieties (Graphene-MoS$_2$) we performed a topological analysis of the electron density by means of the Bader procedure\textsuperscript{49,50} as implemented in CRITIC2.\textsuperscript{51,52} See Supporting Information for further details.\textsuperscript{22,27,53,62–75}

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Supporting Information Available

Experimental and theoretical methods, additional Raman data, additional photoluminescence data, atomic force microscopy measurement, additional DFT results.

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Graphical TOC Entry

MoS$_2$-covered G-FET
G-contacted MoS$_2$-FET
Si p++
Si p++
SiO$_2$ 300nm
SiO$_2$ 300nm
Cr/Au Cr/Au
MoS$_2$Gr
MoS$_2$Gr