Metal-insulator transition in monolayer MoS$_2$ via contactless chemical doping

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Abstract

Much effort has been made to modify the properties of transition metal dichalcogenide layers via their environment as a route to new functionalization. However, it remains a challenge to induce large electronic changes without chemically altering the layer or compromising its two-dimensionality. Here, a non-invasive technique is used to shift the chemical potential of monolayer MoS$_2$ through p- and n-type doping of graphene (Gr), which remains a well-decoupled 2D substrate. With the intercalation of oxygen (O) under Gr, a nearly rigid Fermi level shift of 0.45 eV in MoS$_2$ is demonstrated, whereas the intercalation of europium (Eu) induces a metal–insulator transition in MoS$_2$, accompanied by a giant band gap reduction of 0.67 eV. Additionally, the effect of the substrate charge on 1D states within MoS$_2$ mirror-twin boundaries (MTBs) is explored. It is found that the 1D nature of the MTB states is not compromised, even when MoS$_2$ is made metallic. Furthermore, with the periodicity of the 1D states dependent on substrate-induced charging and depletion, the boundaries serve as chemical potential sensors functional up to room temperature.

Metalllic transition metal dichalcogenide (TMDC) monolayers show a plethora of many-body phenomena, such as charge density wave order [1], Mott insulating states [2] or superconductivity [3]. Understanding these correlated phases, as well as their dependence on external electric or magnetic fields, allows the creation of devices with tunable phase transitions [4]. While intrinsic TMDC metals are being extensively investigated, less is known about the metallic properties of intrinsic TMDC semiconductors such as MoS$_2$ and WS$_2$, mainly due to experimental difficulties in shifting the chemical potential close to the conduction or valence band.

Monolayer MoS$_2$ and WS$_2$ have electronic band gaps of more than 2.0 eV when resting on weakly interacting substrates (see [5] for a discussion of substrate-induced band gap variability in MoS$_2$). Hence, back-gated devices are typically unable to bring the chemical potential close to the onset of the conduction or valence band before breakdown occurs [6, 7]. Larger shifts are obtained with ionic-liquid-gating. With this method, transport measurements showed that MoS$_2$ and WS$_2$ become superconducting when the chemical potential lies within the conduction band [8–13]. However, ionic-liquid-gating suffers from charge inhomogeneities [14]. At low temperatures this effect is exacerbated due to freezing of the liquid [15, 16]. The liquid also hampers complementary measurements using surface sensitive techniques. As a consequence, many open questions remain on the nature of the superconducting dome in MoS$_2$ [8–10, 17, 18] and WS$_2$ [12], the origin of the finite density of states within the superconducting gap [19], and on the properties of the (quasi-) metallic phase in between the insulating and superconducting phases [12].
Another method to obtain large shifts of the chemical potential is the introduction of foreign species. This is done through adsorption, elemental substitution or via intercalation between the 2D sheet and its substrate [20–25]. But the direct contact with the TMDC results in, like in the case of ionic-gating, an entangled effect of charge redistribution and chemical hybridization [26], leading to non-universal, element-specific properties. Hence, an efficient method able to tune the chemical potential of TMDs by large amounts without chemically altering it or leaving the surface inaccessible would be highly desirable. Such a method would make it possible to gain fundamental knowledge on the effect of charge on the band structure of TMDC semiconductors [13], ultimately enabling access to novel phases of matter, such as topological superconductivity [27].

Here, we introduce contactless chemical doping as a method to induce large shifts in the chemical potential of MoS$_2$, without disturbing its chemical environment. We chemically dope a Gr layer from below in order to shift the chemical potential of MoS$_2$ monolayer grown on top in situ. The doping is done through the use of intercalants, taking Eu and O as electron donor and acceptor respectively, to create high quality MoS$_2$/Gr/(Eu or O)/Ir(111) layered configurations. For both intercalants, it has been found that they are able to cause considerable shifts in the Dirac point of Gr (as far as $E_D = -1.38$ eV for Eu and up to $E_D = +0.68$ eV for O), without strong hybridization [28–31]. In this way, the chemical potential within the MoS$_2$ band structure can be controlled through the doping level of Gr and shifted far beyond what is possible in traditional back-gate device setups, without hybridization or loss of surface accessibility and quality. The MoS$_2$/doped Gr samples are analyzed experimentally with scanning tunneling microscopy (STM) and spectroscopy (STS) and theoretically with ab initio density functional theory (DFT) calculations. Additional attention is given to the effect of the Gr doping on the 1D states within mirror-twin boundaries (MTBs) in MoS$_2$, which can be filled and depleted via the substrate without compromising their 1D nature. Thereby, they can be used as chemical potential sensors.

1. Results

1.1. Metal–insulator transition in MoS$_2$

Our method is illustrated in figure 1(a). The initial heterostructure consists of three different materials: the 2D semiconductor MoS$_2$, the 2D semi-metal Gr, with the Dirac point close to Fermi level $E_F$, and the metallic Ir(111). Since foreign elements bind much more strongly to Ir(111) than to the van der Waals materials Gr and MoS$_2$, this arrangement enables us to intercalate these between Gr and Ir(111), while preserving the chemical environment of MoS$_2$. Here, the concept is demonstrated for the case of Eu and O.

Intercalating an electron donor such as Eu thus leads to an upward shift of the chemical potential in Gr via charge transfer. Similarly, the intercalation of an electron acceptor such as O causes the chemical potential of Gr to shift down in energy. These changes in the Gr substrate cause comparable shifts in the chemical potential of the top layer via workfunction alignment and/or charge transfer. The precise mechanisms by which the MoS$_2$ chemical potential is shifted for each intercalant will be discussed in detail below. In the following, we refer to MoS$_2$/Gr/Eu/Ir(111) (MoS$_2$/Ir(111)) as MoS$_2$ on n-doped (p-doped) Gr, while MoS$_2$/Gr/O/Ir(111) is referred to as pristine.

The STM topograph of figure 1(b) displays the pristine sample as a reference. Islands of monolayer (ML) MoS$_2$ are distributed on the Gr/Ir(111) substrate. The typical apparent height of the ML islands is 0.65 nm when tunneling into the MoS$_2$ conduction band. Apart from MTBs, which appear as bright lines, defects are largely absent. In the inset, an atomic resolution topograph of MoS$_2$ shows that the moiré of Gr/Ir(111) is visible through the MoS$_2$ layer, see SI (figure S2). This system has previously been investigated in detail in [5].

An STM image of MoS$_2$ on p-doped Gr is shown in figure 1(c). O was intercalated after the growth of MoS$_2$, as the O would etch Gr at the high temperatures employed in MoS$_2$ growth. The process is detailed in the section 3. The Gr layer is partially combusted, leaving uncovered areas (holes) in the graphene sheet, while the O atoms intercalate the subsisting Gr. An area where Gr was combusted is partly imaged in the top right of figure 1(c). After the process extended Gr patches remain, on which MoS$_2$ is found. The Gr layer is completely intercalated with a O-(2$\sqrt{3}$×2$\sqrt{3}$)-R30$^\circ$ superstructure reported previously, see SI (figure S1) [33]. Since O-intercalation decouples Gr from Ir(111), the Gr/Ir(111) moiré...
Figure 1. (a) Side view schematics visualizing the method of achieving large chemical potential shifts of MoS$_2$ on Gr/Ir(111). Left: pristine MoS$_2$. Middle: MoS$_2$ on p-doped Gr through post-growth O intercalation under Gr. Right: MoS$_2$ on n-doped Gr through pre-growth intercalation of Eu under Gr. (b)–(d) Constant current STM overview topographs of: (b) MoS$_2$/Gr/Ir(111); (c) MoS$_2$/Gr/O/Ir(111) and (d) MoS$_2$/Gr/Eu/Ir(111). (b) Sample sparsely covered by ML MoS$_2$. A single Ir(111) step edge is visible in the top left. The atomic resolution inset shows the moiré of Gr on Ir(111) imaged through the MoS$_2$. (c) Sample sparsely covered by ML MoS$_2$; no bilayers have formed. On the right, Ir(111) is not covered by Gr. The atomic resolution inset shows the appearance of a MoS$_2$/Gr moiré. (d) Sample largely covered by ML MoS$_2$, with close to no bilayers present. Gr appears in two phases, bare (dark) and Eu-intercalated (brighter). As is highlighted by the inset, no Gr/Ir(111) moiré appears in the MoS$_2$ layer.

STM parameters ($V$, $I$): (b) 1.0 V, 0.05 nA; (c) 3.5 V, 0.01 nA; (d) 1.0 V, 0.10 nA; (b)–(d) image size 150 × 150 nm$^2$. Insets: (b) 0.5 V, 0.58 nA; (c) 1.0 V, 0.10 nA; (d) 1.0 V, 0.10 nA; (b)–(d) image size 6.3 × 6.3 nm$^2$.

A moiré vanishes and a moiré between MoS$_2$ and Gr becomes visible as shown in the inset of figure 1(c).

Figure 1(d) is an STM topograph of the surface morphology of MoS$_2$ on n-doped Gr. The Gr layer not covered by MoS$_2$ is not uniformly intercalated: large intercalation areas and stripes of apparent height 0.30 nm are visible, similar to previous Gr/Eu/Ir(111) samples [34]. All investigated MoS$_2$ islands have an apparent height of around 0.70 nm relative to the higher (brighter in d) patches of Gr, under similar tunneling conditions as for the pristine sample, consistent with the absence of any Eu in between Gr and MoS$_2$. We thus infer that ML MoS$_2$ grows preferentially on top of Gr/Eu/Ir(111). A similar preference for adsorption on Eu-intercalated patches was observed for aromatic molecules [35]. The moiré of Gr/Ir(111) is no longer visible in the MoS$_2$ layer; instead, the layer shows slight apparent height modulations, due to a variation in the density of the intercalated Eu underneath Gr, see SI (figures S2 and S3).

We use STS to investigate how the band structure of MoS$_2$ is altered due to doping of the Gr substrate. The spectra in figures 2(a) and (b) are recorded in constant height and constant current mode on MoS$_2$, respectively. Constant height STS, in figure 2(a), is proportional to the local density of states and hence records the band gap position in energy. For pristine MoS$_2$ (black dots), the apparent valence band (VB) and conduction band (CB) edges are close to −1.8 eV and 0.9 eV, respectively. The doping of Gr leads to non-trivial energy shifts of these apparent band edges. The spectrum measured on MoS$_2$ on p-doped Gr displays a nearly rigid upward shift (∼450 meV) of the apparent VB and CB edges (red dots). Since both band edges shifted by approximately the same amount, the p-doping of Gr leaves the MoS$_2$ band gap nearly unchanged with only a minor reduction of ∼20 meV. Upon n-doping, a considerable narrowing of the band gap is found, with the apparent CB edge shifting close to the Fermi energy, while the apparent VB edge remains at approximately the same location (blue dots). The shift of the apparent CB by ∼700 meV demonstrates a large shift of the chemical potential of MoS$_2$, whereas the lack of
Table 1. Critical point energies (eV) identified in ML MoS$_2$ on different substrates using constant current STS (averaged over multiple data sets), and the corresponding distance between the well-defined $\Gamma$ and Q peaks in STS $E_{\Gamma-Q}$. For more details on the MoS$_2$/Gr/Ir(111) data, including the determination of the actual electronic bandgap $E_g = 2.53$ eV, see [5]. The location of the K-point of MoS$_2$ on n-doped Gr has been determined using quasiparticle interference mapping (see figure 3), since it is not accessible via constant current STS.

| MoS$_2$ on   | $\Gamma$  | K       | Q   | $E_{\Gamma-Q}$ |
|--------------|-----------|---------|-----|---------------|
| Gr/Ir(111)   | $-1.87 \pm 0.02$ | $0.77 \pm 0.02$ | $0.90 \pm 0.05$ | $2.77 \pm 0.05$ |
| Gr/Eu/Ir(111)| $-1.90 \pm 0.01$ | $(-0.09 \pm 0.01)$ | $0.20 \pm 0.01$ | $2.10 \pm 0.01$ |
| Gr/O/Ir(111) | $-1.37 \pm 0.04$ | $1.22 \pm 0.03$ | $1.38 \pm 0.03$ | $2.75 \pm 0.05$ |

a significant shift of the apparent VB is indicative of a large band gap renormalization, as will be analyzed in more detail below.

Constant current STS detects the critical point energies in the band structure [5, 36]. It serves as a complementary method to constant height STS. The resulting spectra are shown in figure 2(b). We follow the analysis of [5] to identify the critical point energies of MoS$_2$. In the VB, the $\Gamma$-point band edge states cause a large peak [5], which is found in all three systems. The actual VB maximum at the K-point is not detected in MoS$_2$ because of its large parallel momentum, in-plane orbital character and close proximity in energy. Based on ARPES measurements, the VB K-point was estimated to lie 0.11 eV above the $\Gamma$-point energy of the VB [37, 38]. The CB minimum at the K-point, however, is dominated by out-of-plane orbitals and thus appears as a small shoulder [5, 39]. This shoulder is found in the pristine sample and in MoS$_2$ on p-doped Gr, but cannot be detected in MoS$_2$ on n-doped Gr with constant current STS, as the signal diverges near the Fermi energy. States from the CB Q-point edge cause a larger peak, which is reproducibly found in all three samples. For that reason, we specify the gap size $E_{\Gamma-Q}$, used for determining the renormalization energy, as the energetic distance between the well-defined VB $\Gamma$ peak and the CB Q peak in constant current STS. The actual bandgap is expected to be at least 240 meV smaller, see [5]. The exact location of the critical point energies and estimated $E_{\Gamma-Q}$ gap sizes are listed in table 1.

Remarkably, we find that the CB of MoS$_2$ on n-doped Gr is effectively at the Fermi level. To address this point, we perform STS mapping to investigate the conduction band minimum (CBM) of MoS$_2$ on n-doped Gr. MoS$_2$ patches enclosed by grain boundaries and island edges host confined states, effectively forming a quantum well. Mapping these standing waves allows us to detect the quasiparticles close to the Fermi energy. Figure 3(a) displays STS maps of such a triangular quantum well, in which we identify quantized states [40]. The lowest state is pronounced already at $-50$ meV below the Fermi energy, providing the smoking gun for the metallic nature of MoS$_2$ on this substrate. In addition, more complex states appear at higher energies, as expected for an electron-like band.

Quasiparticle interference patterns around defects and confined quantum well states such as those in figure 3(a) are used to determine the dispersion of the quasiparticles around the Fermi energy. The result is shown in figure 3(b). The different data sets and methods used to obtain these data points are shown and discussed in the SI (figure S4). We fit the data with a parabolic dispersion and find that the bottom of the band is located at $-85 \pm 6$ meV. This is consistent with constant height STS measurements taken with small tip-sample distances, shown in the SI (figure S5). We further obtain an effective mass of $0.36 \pm 0.02 \times m_e$, which agrees with the calculated effective mass of $0.35–0.40 \times m_e$ at the K-point [41, 42].

1.2. DFT calculations and model of band shifts
We conducted DFT calculations to obtain a qualitative understanding of the mechanism through which the shifts of the chemical potential of MoS$_2$ are enabled. Our supercell includes the MoS$_2$ and Gr
sheets, while the Ir(111) substrate was omitted. This simplified model of the experimental situation grasps the essentials at affordable computational effort. We also note that the renormalization of the fundamental bandgap due to screening is not accounted for in our DFT calculations. Since the band alignment is sensitive to strain in MoS$_2$ and Gr, we adopted a supercell model where strain was minimized.

Figures 4(a)–(c) show the structural models of the pristine heterostructure and the intercalated structures containing two O and two Eu dopants, respectively. The figures also show the total charge transfers, as obtained by summing up the Bader charges, and the charge density difference isosurfaces (defined as $\rho$(MoS$_2$/Gr) − $\rho$(MoS$_2$) − $\rho$(Gr) and $\rho$(MoS$_2$/Gr/dopants) − $\rho$(MoS$_2$/Gr) − $\rho$(dopants)). In the case of the pristine heterostructure, the electronic structure at the interface is slightly perturbed by the presence of the other layers, which effectively yields a small charge transfer and an interface dipole induced potential shift of about 0.25 eV. In the case of the O-doped heterostructure, there is significant electron transfer from the Gr to O, while the MoS$_2$ layer is left mostly unaffected. This is in stark contrast to the Eu-doped heterostructure, where we find charge transfer from Eu to both Gr and MoS$_2$, albeit with the charge transfer to Gr still considerably larger. The charge transfer, induced dipoles and Dirac-point positions are listed in the SI (table S1).

Figures 4(d)–(f) show the DFT-calculated local densities of states projected onto the two or three constituent layers. We find that pristine MoS$_2$ is semiconducting, with the Fermi level 0.2 eV below CBM and the gap of 1.69 eV close to the value calculated for an isolated monolayer [43]. Gr remains charge neutral, with the Fermi level coinciding with the Dirac-point, since the interface dipole is the result of modifications to the extensions of the Gr wave functions and not of charge transfer. In the case of the O-doped heterostructure Gr is p-type doped, with the Fermi level 0.58 eV below the Dirac-point and 0.75 eV below the MoS$_2$ CBM. Thus we find a near-rigid shift of the Gr and MoS$_2$ bands to higher energies, in agreement to our experiments. In the case of the Eu-doped heterostructure Gr is n-type doped, with the Fermi level 0.99 eV above the Dirac-point and 0.05 eV above MoS$_2$ CBM. This represents a strong deviation from a rigid shift picture, in which one would expect the Fermi level to lie 0.8 eV above the MoS$_2$ CBM. DFT thus reproduces the metal–insulator transition, as well as the shifts of the Gr Dirac point and MoS$_2$ conduction band found experimentally, including deviations from a rigid shift. Our DFT model thus captures the essence of our experimental observations, although the absence of the Ir substrate leads to a significantly lower density of dopants needed to obtain shifts comparable to the experiments.

The physics involved in the changes of band edge positions and bandgap width can be grasped in a model, accounting for workfunction alignment and interface dipole formation, as shown in figures 5(a)–(c). The MoS$_2$, Gr and Ir(111) band diagrams are sketched for the three samples. Two interfaces are considered: between (doped) Gr and Ir(111), and between (doped) Gr and MoS$_2$. If charge transfer is possible between the layers (e.g. the metal–metal junction between Gr and Ir), an interface dipole will be formed, as a result of workfunction differences.
If no charge transfer is possible because one of the materials is gapped (e.g. the metal–semiconductor junction between undoped Gr and MoS₂), the workfunctions of the two materials have to align through shifts in the position of the chemical potential with respect to the band structure and thus to the vacuum level.

Both types of interfaces are present in the pristine case sketched in figure 5(a). The Ir(111) workfunction $\Phi_{\text{Ir}} = 5.76 \text{ eV}$ [44] is considerably larger than the workfunction of pristine Gr $\Phi_{\text{Gr}} = 4.56 \text{ eV}$ [45]. Due to the difference in workfunctions, charge will flow from Gr to Ir until an interface dipole is formed, halting the flow of further charge carriers. As a result, Gr is slightly p-doped when grown on Ir(111), by about 0.1 eV [46]. Note that for physisorbed Gr with an intact Dirac cone, e.g. Gr on Ir(111), even strong doping does not change the energetic separation of the Dirac point from the vacuum level, it being identical to the workfunction of undoped Gr [47].

When ML MoS₂ is placed on top of Gr, the interface dipole between Gr and Ir is marginally changed due to a slight increase in the p-doping of Gr, from +0.1 eV to +0.25 eV [37], resulting in a Gr workfunction $4.56 \text{ eV} + 0.25 \text{ eV} = 4.81 \text{ eV}$. Between the interior of the MoS₂ layer and Gr no charge transfer is possible, as the Fermi level lies within the MoS₂ band gap. Therefore, with no dipole formed, the workfunctions of both materials have to align. The chemical potential of MoS₂ correspondingly shifts from the middle of the band gap closer to the CB. With the ML MoS₂ electron affinity $\chi \approx 4.0 \text{ eV}$ [48–52], and finding the conduction band edge $E_C$ of MoS₂/Gr/Ir(111) in STS at 0.77 eV, the workfunction of MoS₂ on Gr/Ir(111) $\Phi_{\text{MoS}_2} = \chi + E_{\text{CBM}} = 4.77 \text{ eV}$ is indeed very close to that of Gr: $\Phi_{\text{Gr}} = 4.81 \text{ eV}$.

When O is intercalated underneath Gr, shown in figure 5(b), the Dirac point moves to 0.68 eV [31] and the Gr workfunction changes to $4.56 \text{ eV} + 0.68 \text{ eV} = 5.24 \text{ eV}$. The interface dipole between Gr and Ir(111) becomes smaller. Following the previous considerations, the MoS₂ bands must follow the shift of the Dirac point, in order to keep the workfunctions of Gr and MoS₂ the same. The measured K-point shift in the MoS₂ CB of ≈450 meV is correspondingly close to the expected Gr Dirac point shift of 430 meV. The chemical potential of MoS₂ is thus directly set by that of Gr, as long as MoS₂ remains insulating.

Experimentally, we find that the size of the band gap $E_g$ is only slightly reduced, when comparing the p-doped and pristine sample. Since MoS₂ is still insulating, the screening within the layer should not have changed. Gr, on the other hand, has an increased hole density on the order of $10^{13} \text{ cm}^{-2}$ due to an estimated Dirac point energy $E_D = −0.68 \text{ eV}$ [29]. Gr is thus expected to better screen electrostatic interactions in MoS₂. Previous experimental and theoretical work on TMDC/Gr heterostructures has however found that the effect of increased Gr carrier density on the band gap flattens off after $E_D = \pm 0.25 \text{ eV}$ [7, 53]. Since the Gr layer is already p-doped in the pristine MoS₂ sample [37], the observed renormalization of $\Delta E_g ≈ 20 \text{ meV}$ seems to indicate that the substrate-induced renormalization is already close to saturation prior to O-intercalation.

For Eu-doped Gr, figure 5(c), the situation is decidedly different. Gr/Eu has its Dirac point at about $−1.38 \text{ eV}$, see [28] and the SI (figure S6). The chemical potential difference between Eu-doped Gr and pristine MoS₂ is larger than the difference between pristine MoS₂ and the pristine CB edge. The MoS₂ potential will therefore shift in response to the Eu-doped Gr potential until it hits the CB and MoS₂ becomes metallic. Charge flows from Gr to MoS₂, creating an interface dipole, which reduces the shift of the MoS₂ CB minimum compared to the shift of the Dirac point of graphene.

In addition to the formation of an interface dipole, the charge carriers within MoS₂ are also able to efficiently screen within the layer, leading to the experimentally observed band gap reduction $\Delta E_g = 0.67 \text{ eV}$. The renormalization of the bandgap
Figure 6. Confined states along 4|4E and 4|4P MTBs in ML MoS\(_2\) on different substrates. (a) Ball-and-stick model of a 4|4E MTB. Mo atoms are navy, S atoms yellow (top layer) or dark yellow (bottom layer). A MoS\(_2\) lattice vector is indicated. (b) Constant current STM topograph of a 4|4E MTB in MoS\(_2\) on Gr/Ir(111). (c) Constant height STM image of a 4|4E MTB in pristine (–), p-shifted (O) and n-shifted (Eu) MoS\(_2\). Vertical white lines are a guide to the eye. (d) Dispersion of the hole-like 1D band of the 4|4E MTB, with data from MTBs on the differently doped Gr substrates in their respective colors. In green a DFT-calculated dispersion for MoS\(_2\)/Gr/Ir(111) is shown, taken from [59]. Experimental data from spectra taken along the same MTBs as used for the averaged linescans in (f)–(h). (e) Plot of 4|4E (gray) and 4|4P (teal) MTB beating periodicity near \(E_F\) versus the location of the CBM. The dotted lines are a guide to the eye. (f)–(h) Constant height STS linescans along a 4|4E MTB in MoS\(_2\)/Gr/Ir(111) (left), MoS\(_2\)/Gr/O/Ir(111) (middle) and MoS\(_2\)/Gr/Eu/Ir(111) (right). The spectra are averaged over the whole length of the MTB. Indicated is the ratio of the gap at the Fermi level (\(E_{\text{gap}}\)) with respect to the average gap between the quantized states (\(E_{\text{qws}}\)).

STM/STS parameters: (b) top panel: \(V = 1.25\) V, \(I = 0.02\) nA; (b) –: \(V = 0.10\) V, \(I_{\text{st}} = 0.5\) nA; O: \(V = 0.02\) V, \(I_{\text{st}} = 0.1\) nA; Eu: \(V = 0.20\) V, \(I_{\text{st}} = 0.05\) nA; 1 nm scale bar shown. (f) \(V_{\text{st}} = 0.5\) V, \(I_{\text{st}} = 0.1\) nA; (g) \(V_{\text{st}} = 0.5\) V, \(I_{\text{st}} = 0.1\) nA; (h) \(V_{\text{st}} = -0.5\) V, \(I_{\text{st}} = 0.1\) nA.

due to the metal–insulator transition is considerably larger than what is achieved via methods which only increase the carrier density in the substrate. In those cases, renormalization energies of at most 0.24 eV have been reported [7, 54].

1.3. Effect of charge on mirror twin boundaries

The presence of 0D defects (such as vacancies) or 1D defects (such as MTBs) in TMDCs will influence the shifts of the chemical potential induced via contactless chemical doping. In-gap states within these defects tend to weaken the impact of the work function difference due to local Fermi level pinning [55–57], which is absent away from these defects [58]. In the pristine sample, the presence of in-gap states below the Gr Fermi level in MoS\(_2\) edges and MTBs leads to the accumulation of charge in the MTBs, causing band bending in the surrounding semiconductor [59]. With the doping of Gr potentially influencing the amount of charge that is transferred to the MTBs as well as the dielectric properties of the MoS\(_2\)/Gr heterostructure (e.g. by inducing a metal–insulator transition), it is worthwhile to disentangle the various effects of Gr doping on the MTB states and the electronic landscape surrounding them.

In MoS\(_2\) two types of MTBs (4|4E and 4|4P) are present, formed between 180°-misoriented MoS\(_2\) domains [60, 61]. A model and a constant current STM image of the 4|4E MTB are shown in figures 6(a) and (b), respectively. The 4|4P MTB is discussed in the SI (figure S4). In the pristine sample, the states within MTBs are strictly 1D, leading to strong electron-correlations and the emergence of Tomonaga–Luttinger liquid (TLL) behaviour [62]. In addition, since the states are located in boundaries of finite length, they are confined. Hence, when mapping the local density of states close to the Fermi energy, we expect a pronounced, sinusoidal beating pattern along the length of the MTB, resulting from quantized 1D electronic states, as shown in figure 6(c). The wavelength of this beating pattern is related to the confined states closest to the Fermi energy, \(\lambda = \pi/k_F\) [62]. Therefore, if the charge donated by the Gr substrate shifts the Fermi level of the MTB band, the change in filling can be observed directly with STM, by imaging the periodicity of the states near \(E_F\).

The constant height STM images in figure 6(c), taken near \(E_F\), reveal the beating patterns found within 4|4E MTBs for MoS\(_2\) on the differently doped substrates. In the pristine case, we find \(\lambda^{44E} = (2.01 \pm \ldots\))
ary, the Fermi level sinks to charge in the boundary is given in the SI (table S2). For p-shifted MoS$_2$, the periodicity along the 4|4E MTBs has visibly decreased, $\lambda_F^p = (1.72 \pm 0.01) \, a$, while for n-shifted MoS$_2$, an increased periodicity of $\lambda_F^n = (2.69 \pm 0.11) \, a$ is measured.

The shifts in the beating periodicity can be understood from the band structure of the MTB. 4|4E MTBs host a hole-like band, which is shown in green in figure 6(d), based on DFT calculations discussed in [62]. With the Fermi level $E_F$ in the pristine case bisecting the band at $k_F = \pi/2a$, this leads to the observed $2 \, a$ periodicity. When the Gr substrate is n-doped, additional charge can flow into the boundary, raising the Fermi level to $E_F^p$ and leading to an increased wavelength $\lambda_F^p$. For p-doping of Gr, the inverse happens: charge is extracted from the boundary, the Fermi level sinks to $E_F^n$ and $\lambda_F^n$ decreases. The quantitative relationship between $k_F$ and the line charge in the boundary is given in the SI (table S2).

From the measured $k$ values we find that the chemical potential shifts in the MTB are considerably smaller than those in Gr or MoS$_2$, with the Fermi level difference between the 4|4E on n- and p-doped Gr about 500 meV, see SI (table S2) for the exact values. In other words, the states within MTBs locally pin the Fermi level, while Fermi level pinning is absent in MoS$_2$ away from defects. This can be understood from previous considerations: the metal-metal interface between the MTB and Gr allows for charge transfer and thus the formation of an interface dipole. As a consequence, the MTB Fermi level will not shift as much as the chemical potential of MoS$_2$, which rigidly follows the Gr doping level until it becomes metallic. Note that the relation between $\lambda_F$ and Fermi level is reversed for 4|4P MTBs, which host an electron-like band, see SI (figure S7).

Our findings are summarized in figure 6(e) in which we plot the position of the CBM of MoS$_2$ as a function of beating period for the two types of MTBs. This allows the identification of the Fermi vector of the MTB band and the position of the chemical potential $\mu$ with respect to the MoS$_2$ conduction band in a single STM image. Due to the close proximity of CBM and chemical potential in our n-shifted MoS$_2$ samples, we can also set a lower bound of $\lambda_F^n = (2.69 \pm 0.11) \, a$ for the beating pattern within 4|4E MTBs, for which the surrounding 2D material is metallic. As a consequence, the MTBs function as a sensor—they allow for a determination of the chemical potential of MoS$_2$ by measuring the periodicity of the MTB states near $E_F$. This method is also applicable at room temperature.

In figures 6(f)–(h) we display additional constant height STS linescans averaged along the length of 4|4E MTBs on all three substrates, respectively. The finite length of the MTBs leads to a series of peaks in the $dI/dV$ spectra at the energetic location of the quantized states. The dominant lowest energy excitations for a given wavevector are used to obtain the dispersion within the 4|4E MTBs, see figure 6(d) [62]. We find a pronounced gap $E_{\text{gap}}$ around the Fermi level, consistent with the presence of a Coulomb blockade which pushes the states closest to $E_F$ further apart [62]. The gap is almost twice as large as the energy spacing between the quantized states $E_{\text{qws}}$. We find that the ratio $E_{\text{gap}}/E_{\text{qws}}$, which eliminates the length-dependence of both parameters [64], has only minor substrate-dependence. This is surprising, since the presence of a Coulomb gap, which arises from strong electron–electron interactions, indicates that the 1D correlated states within 4|4E MTBs persist even when the surrounding MoS$_2$ is metallic.

Moving away from the effects of the intercalation on the intrinsic MTB properties, we also investigated the region directly surrounding the boundaries, where the MoS$_2$ bands are bent under the influence of the MTB charge [59]. The magnitude of band bending must change if the amount of charge on the MTB is changed in consequence of Gr doping, while the shape of the bending provides insight into how the screening properties of MoS$_2$ are affected.

For reference, we take constant current STS linescans orthogonally crossing a 4|4E MTB in the pristine heterostructure. While figure 7(a) captures the behaviour of the CB edge, figure 7(b) captures that of the VB. Far away from the MTB, at $x = \pm 5 \, \text{nm}$, the unperturbed pristine band structure is observed. Approaching the MTB, located at $x = 0 \, \text{nm}$, both CB and VB are seen to bend upwards by at least 0.5 eV, indicating that the MTB is negatively charged. The bending is smooth in the CB but occurs stepwise at characteristic energies in the VB due to quantization effects [59].

On p-doped Gr, figures 7(c) and (d), the magnitude of the bending is severely reduced for both bands, while the spatial extent of the bending is similar to that of the pristine case. There are fewer quantized VB levels and the unperturbed band structure is recovered at $x = \pm 4 \, \text{nm}$. This can be understood from previous considerations: Gr is more p-doped, lowering its chemical potential. As a result, certain MTB states are now shifted above the Gr Fermi level and less charge can flow from Gr into the MTB, reflected in its smaller periodicity at $E_F$.

On n-doped Gr, shown in figures 7(e) and (f), the bending of the MoS$_2$ bands occurs in a much smaller range of $|2| \, \text{nm}$ on either side of the MTB. In figure 7(f) there are fewer quantized VB levels—only two—and their energy spacing is larger. The highest quantized state occurs at around $-1.3 \, \text{eV}$, compared to $-1.0 \, \text{eV}$ found in the pristine sample. Additionally, the VB bends up steeply at $x \approx \pm 1.5 \, \text{nm}$ from the boundary. The increase in band bending due to graphene n-doping is expected, as more charge is transferred into the MTB states.

The decrease of the spatial extent of band bending on the one hand is a sign of the metallic phase.
of MoS$_2$ on Gr/Eu/Ir(111), which effectively screens the charge within the MTB. On the other hand, the steep band bending close to the MTB leaves the direct surrounding of the latter insulating, in line with the persistent Coulomb gap $E_{\text{gap}}$ found experimentally.

2. Discussion

We have demonstrated a non-invasive method to strongly modify the electrostatic environment of ML MoS$_2$, applicable also to other TMDCs and van der Waals materials. We have shown that the doping of its Gr substrate can induce a metal–insulator transition in MoS$_2$ and enables the manipulation of metallic states within MTBs. In addition, the chemical potential shifts in MoS$_2$ can be monitored via MTB states and the screening environment around the boundaries. The backside functionalization of Gr leaves the TMDC top layer chemically pristine, thereby offering advantages over chemical doping or adatom techniques. Our contactless chemical doping method to shift the chemical potential of wide-bandgap semiconductors can be extended by other intercalants such as alkalis [65], other rare earth metals [66] or the p-dopant chlorine [67]. Continuous tuning of the chemical potential, analogous to gating, could be accomplished by using Li as intercalant [68, 69]. A combination of contactless gating for coarse adjustment of the chemical potential with electrostatic gating for fine adjustment represents another exciting perspective. As the conductive Gr substrate is not suited to most technological applications, replacing it with an insulating layer such as hexagonal boron nitride presents a promising layer such as hexagonal boron nitride presents a promising approach to achieve practical implementation of this method. We envision that contactless chemical doping will enable observation and characterization of novel states of matter using both local and global surface science techniques.

3. Methods

The samples were grown in situ in a preparation chamber with base pressure $p < 5 \times 10^{-10}$ mbar. Ir(111) is cleaned by 1.5 keV Ar$^+$ ion erosion and annealing to temperatures $T \approx 1550$ K. Gr is grown on Ir(111) by two steps. First, room temperature ethylene exposure till saturation followed by 1370 K thermal decomposition gives well-oriented Gr islands. Second, exposure to 2000 l ethylene at 1370 K for 600 s yields a complete single-crystal Gr layer [70]. ML MoS$_2$ is grown by Mo deposition in an elemental S pressure of $1 \times 10^{-8}$ mbar [71]. Subsequently, the sample is annealed to 1050 K in the same S background pressure. The Eu-intercalated sample is prepared in the order: Gr growth; Eu intercalation; MoS$_2$ growth. Eu is evaporated from a Knudsen cell onto the Gr/Ir(111) crystal kept at 720 K. Intercalation is confirmed by low-energy electron diffraction (LEED) [72]. After Eu intercalation no Eu is adsorbed on.
Gr [72, 73]. Subsequently, the sample is annealed to 1075 K. Due to this annealing step, all Eu that could escape from underneath the Gr at the lower MoS2 annealing temperature of 1050 K has already escaped. Thereby Eu contamination of MoS2 during subsequent MoS2 growth and annealing is prevented. The O-intercalated sample is prepared in the order: Gr growth; MoS2 growth, O intercalation. O intercalation is achieved by exposing MoS2/Gr/Ir(111) for 210 seconds at 770 K to 2 × 104 l of O2 [30, 33]. No obvious increase in the density of point defects, such as oxygen substitutions [74], is observed in MoS2 after oxygen intercalation.

STM and STS are carried out in the T = 7 K bath cryostat system after in situ transfer from the preparation chamber. STS is performed with the lock-in technique, at modulation frequency 619–777 Hz and modulation voltage Vmod = 4 mVrms, with an experimental resolution of ≈10 meV or better [75]. We employ constant height (recording (dI/dV)) and constant current ((dI/dV)) STS modes, where I is the tunneling current, V the bias voltage, and Z the tip-sample distance or height. In both modes dI/dV is recorded while V is ramped; see [3] for further explanation. Spectra are always taken away (>6 nm) from defects, unless indicated otherwise.

All density functional theory calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) [76, 77]. The plane wave cutoff was set to 400 eV throughout. We used the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) [78]. Van der Waals interactions are described using Grimme’s semi-empirical corrections [93]. A 4 × 4 k-point mesh was used during structural optimization in the supercell, while the density of states is evaluated using a 16 × 16 mesh. The optimized lattice constants of MoS2 and Gr are 3.18 Å and 2.468 Å, respectively. For a minimally strained heterostructure model, we used the same approach and model as in [39], wherein a 4 × 4 supercell of MoS2 is interfaced with a (6,3) × (6,3) Gr cell (i.e. \( \pi_{sc} = 6\pi + 3\tau \), where \( \pi \) and \( \tau \) are the lattice vectors of Gr at an 120° angle). The dopants were placed as far from each other as possible within the supercell. The optimized geometry for O atoms was between graphene top- and hollow-sites. The optimized geometry for Eu atoms was on the graphene hollow site. The MoS2 layer is kept unstrained and Gr layer is compressively strained by 0.8%. Finally, in order to avoid the buckling of Gr due to chemical interactions with the dopants, charging, or strain, the z-coordinates of C atoms were fixed.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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