Universal Fermi-Level Pinning in Transition-Metal Dichalcogenides

Kai Sotthewes, Rik van Bremen, Edwin Dollekamp, Tim Boulogne, Krystian Nowakowski, Daan Kas, Harold J. W. Zandvliet, and Pantelis Bampoulis

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ABSTRACT: Understanding the electron transport through transition-metal dichalcogenide (TMDC)-based semiconductor/metal junctions is vital for the realization of future TMDC-based (opto-)electronic devices. Despite the bonding in TMDCs being largely constrained within the layers, strong Fermi-level pinning (FLP) was observed in TMDC-based devices, reducing the tunability of the Schottky barrier height. We present evidence that metal-induced gap states (MIGS) are the origin for the large FLP similar to conventional semiconductors. A variety of TMDCs (MoSe₂, WSe₂, WS₂, and MoTe₂) were investigated using high-spatial-resolution surface characterization techniques, permitting us to distinguish between defected and pristine regions. The Schottky barrier heights on the pristine regions can be explained by MIGS, inducing partial FLP. The FLP strength is further enhanced by disorder-induced gap states induced by transition-metal vacancies or substitutionals at the defected regions. Our findings emphasize the importance of defects on the electron transport properties in TMDC-based devices and confirm the origin of FLP in TMDC-based metal/semiconductor junctions.
Defects in TMDCs. Figure 1a shows topographic AFM and lateral force images (see the inset of Figure 1a) of a freshly cleaved MoSe₂ surface. The surface appears smooth and defect-free in both images. However, within the simultaneously recorded C-AFM image, the surface is inhomogeneous when a negative voltage is applied to the sample. Multiple dark circular features (with radii ranging between 3 and 4 nm) appear (see Figure 1b). The current recorded at these features is higher than that for the pristine surface. The density of the features varies between 10¹⁰ and 10¹¹ cm⁻² dependent on the sample and location. Imaging a region without round depressions requires a high magnification of a small area. Figure 1c shows an example of a high-resolution STM image where the atomic structure of WSe₂ is observed, revealing the expected hexagonal pattern with a unit cell of (0.33 ± 0.02) nm. The structure is consistent with the semiconducting 2H phase. In addition to the observed hexagonal pattern, several missing atoms are observed. At these positions, Se atoms are missing, inducing Se vacancies. The electronic influence on the TMDCs, a reduction of the extrinsic factors, such as defects and stacking faults, is a prerequisite.

Several works have been conducted to find the origin of FLP and subsequently control its strength. Theoretical studies predicted that the FLP effect in the MSJ is mainly induced by two interface effects: first, due to modification of the metal’s work function by dipole formation at the interface and second, by the introduction of gap states due to the reduction of the chalcogen/transition-metal bonding strength. Later, Guo et al. performed simulations for several TMDCs, showing that the TMDC/metal junctions largely follow the MIGS model, similar to three-dimensional semiconductors despite their different structure and bonding. However, it is difficult to experimentally access the pinning mechanism because of the high density of surface defects, which alter the properties of these materials. To experimentally confirm the pinning mechanism of the TMDC-based MSJ, a defect-free MSJ has to be constructed.

Recently, nanoscopic MSJs have been obtained using conductive atomic force microscopy (C-AFM). In C-AFM, the tip can act as a nanoscopic metal electrode. Characteristics recorded with a C-AFM of the Pt-coated tip/MoS₂ junction revealed variations in the SBH. This method was also used to investigate the effects of local defects, stacking faults, plasma functionalization, and charge variations due to doping on the charge transport across the MSJ. Because of the nanoscopic size of the contact metal, small variations at the surface can be measured. Substitution or removal of the transition metal or the chalcogen atoms lead to defect sites with different electronic properties compared to the pristine regions including small SBH and strong FLP. On MoS₂, defects located at the Mo layer enhance further the FLP strength compared to pristine surface or regions with S-vacancies.

In this work, we use the C-AFM to construct nanoscopic MSJs on several TMDCs, in order to investigate the exact mechanism behind FLP on TMDCs. We performed high-spatial-resolution C-AFM and scanning tunneling microscopy (STM) imaging in order to characterize defects present on several TMDC surfaces (MoSe₂, WSe₂, WS₂, and MoTe₂). For the studied TMDCs, we find defects with similar appearance and influence; STM reveals that chalcogen defects have almost no influence on their surroundings, whereas transition-metal defects lead to a strong localized contrast that depends on the used set point. The barrier heights of the pristine surface can be explained by the MIGS mechanism, which normally applies to three-dimensional semiconductors. Spatially resolved Schottky barrier maps reveal a decrease of the SBH and a stronger FLP at defect sites because of DIGS. The DIGS decrease the pinning factor by approximately 30–40%. Our results provide new insights into the physics governing the contact properties and charge transport through the TMDC-based MSJ.

RESULTS AND DISCUSSION

Figure 1. (a) Topographic AFM image (inset: corresponding lateral force image) of a freshly cleaved MoSe₂ crystal (600 × 600 nm², the scale bar is 200 nm). (b) Simultaneously recorded C-AFM image recorded at −1.2 V sample bias. (c) STM topography image of the WSe₂ surface, revealing missing selenium atoms (10 × 10 nm², the scale bar is 3 nm). The tunneling parameters are 1.1 nA and −0.6 V. (d) STM topography image of dark circular features (30 × 30 nm², the scale bar is 8 nm, tunneling parameters: 100 pA and 1.5 V). (e) Current cross section recorded with C-AFM at the dark round features induced by defects in the first and second trilayers, respectively (inset: the C-AFM image indicating the defects where the cross section was taken (20 × 20 nm², SB is 1.2 V)).
surrounding of the Se vacancies is small (<1 nm in radius), excluding them from being the origin of the dark round features in the C-AFM image (see Figure 1b). Besides, the density of the Se vacancies (10^{12} to 10^{13} cm^{-2}) is 2 orders of magnitude higher compared to that of the dark circular features (10^{10} to 10^{11} cm^{-2}) observed in the C-AFM.

Large-scale STM images reveal the presence of dark depressions similar to the ones observed in the C-AFM (Figure 1d). High-resolution STM images show a depression without disrupting the atomic lattice, confirming that the effect is purely electronic (see the Supporting Information). The average defect density of 10^{10} to 10^{11} per cm^{-2} is comparable to the density found in the C-AFM images. The appearance and density of the defects are very similar to the defects observed on MoS_2. In these studies, the origin of the dark round features was attributed to metal-like defects or impurities located underneath the outermost S layer. Mo-vacancies and antisite (Mo-substitutional) defects occur on the subsurface without a structural modification of the top S layer. These defects ionize the sulfur atoms. Coulomb repulsion around these sulfur atoms leads to electron depletion and causes the appearance of the dark disk observed in both C-AFM and STM. We note here that the observed defects are intrinsic in nature, as the samples have not gone through any treatment (except exfoliation) prior to scanning. In addition, similar features with similar densities were found in other types of TMDCs, such as WS_2 and WSe_2, attributed to impurity atoms (such as Re, Na, and Li) present in the crystal. Therefore, we suggest that the dark circular features originate from metal-like defects (Mo/W vacancies or substitutionals), which change the electronic landscape of their surroundings. Next to the dark circular defects, bright defects are observed in the STM image (Figure 1d). These defects are attributed to trapped electron states around a donor on the surface chalcogen atom layer. However, these defects are not observed in the C-AFM images.

A closer look at the metal-like defects reveals that they fall into two categories: defects with current amplitudes of approximately −150 and −50 pA (at a bias voltage of 1.2 V), as shown in Figure 1e. These differences are caused by the position of the metal-like defect. When located in the top MoSe_2 trilayer, the electronic influence is larger compared to defects located in the second MoSe_2 trilayer, as observed previously for MoS_2 and conventional semiconductors. These results suggest that the conductance of MoSe_2 can be influenced by metal-like defects in the first and second trilayers.

Similar defects are found in the C-AFM images on WS_2, WSe_2, and MoTe_2 (see the Supporting Information). These defects have similar appearances as the metal-like defects on MoS_2 and MoSe_2 (see Figure 1b). Earlier studies emphasized the similarities between the defect types in the different TMDCs. The energies needed to create defects within the different types of semiconducting TMDCs are comparable as well as the structural conformations. Therefore, we conclude that the defects observed with C-AFM on the studied TMDCs are all metal-like defects.

**SBHs on Pristine and Defected Regions.** Because it is now possible to distinguish between defected and pristine regions (note here that the pristine regions still contain chalcogen defects), the local electron transport through nanoscopic MSJ between a Pt tip (ϕ_M = 5.64 eV) and the semiconducting TMDC can be investigated. For zero charge transfer in the MSJ (Schottky limit), the electron SBH is given by

\[ \phi_B = \frac{2 \pi}{\hbar} \ln(M) \]

where \( M = 5.64 \text{ eV} \) and the exponential function is given by

\[ \exp(-\phi_B/\kappa T) \]

The ideality factor (\( \eta \)) is obtained from the logarithmic \( I(V) \) curves from which the SBH is extracted. The spatially resolved current map (200 × 200 nm², scale bar 50 nm) obtained via 128 × 128 individual current–voltage curves, recorded from −0.6 to 1.5 V. The map corresponds to a voltage of −0.15 V. Extracted SBH map of the surface obtained from the individual \( I(V) \) curves in (a). Significant differences in the SBH are observed at the positions of the defects in (b).

Figure 2. (a) \( I(V) \) curves recorded with a Pt tip on a pristine (red) and defected (black) region of MoSe_2. Inset: the corresponding semi-logarithmic \( I(V) \) curves from which the SB is extracted. (b) Spatially resolved current map (200 × 200 nm², scale bar 50 nm) obtained via 128 × 128 individual current–voltage curves, recorded from −0.6 to 1.5 V. The map corresponds to a voltage of −0.15 V. (c) Extracted SBH map of the surface obtained from the individual \( I(V) \) curves in (a). Significant differences in the SBH are observed at the positions of the defects in (b). For the ideality factor (\( \eta \)) map, see the Supporting Information. (d) Histogram of the SBH for the white dashed box marked in (c). Three peaks are observed: (0.37 ± 0.03), (0.30 ± 0.02), and (0.24 ± 0.03) eV for the pristine region, defects located in the second trilayer and defects located in the first trilayer, respectively.
by the difference between the work function of the metal \((\phi_M)\) and the electron affinity of the semiconductor \((\chi_S)\)

\[
\phi_b = \phi_M - \chi_S \tag{1}
\]

A characteristic \(I(V)\) curve for the MoSe\(_2\)-based MSJ is shown in Figure 2a. The measured \(I(V)\) curve on the pristine region shows a diode-like behavior, as expected for a MSJ.\(^{53}\) The negative sample bias is defined as the forward bias regime. For larger negative voltages, the SBH lowers and the current increases exponentially with the voltage. The current in the MSJ under forward bias is described by the thermionic emission model and is given by\(^{54}\)

\[
I = I_0 \exp\left(\frac{-qV}{nk_BT}\right) 1 - \exp\left(-\frac{-qV}{k_BT}\right) \tag{2}
\]

where \(V\) is the applied bias, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(\eta\) is the ideality factor, this is the deviation of the current transport from ideal thermal emission, and \(q\) is the electron charge. For values of \(V\) larger than \(3k_BT/q\), the second term in eq 2 becomes negligible. The reverse saturation current \((I_0)\) is a constant and depends on the Schottky barrier \(\phi_B\)

\[
I_0 = A*A*T^2 \exp\left(-\frac{q\phi_B}{k_BT}\right) \tag{3}
\]

with \(A\) being the MSJ area, that is, the tip contact area and \(A^*\) is the Richardson constant \(\left(A^* = \frac{4q^2\pi m^*}{h^2}\right)\), with \(m^*\) the effective mass and \(h\) the Planck constant. The contact area of the Pt tip is estimated using the Hertz model\(^{55,56}\) and is approximately 2.7 nm\(^2\) at a load of 5–10 nN. The ideality factor is obtained from

\[
\eta = \frac{q}{k_BT} \frac{dV}{d\ln I} \tag{4}
\]

and the \(\phi_B\) for electron injection is acquired using

\[
\phi_B = \frac{k_BT}{q} \ln\left(\frac{A^*AT^2}{I_0}\right) \tag{5}
\]

The ideality factor is extracted from the slope of the linear part of the ln \(I(V)\) curve (like in the inset of Figure 2a). The intercept of this fit gives the saturation current which is used to extract the SBH according to eq 5. By applying the abovementioned equations to the recorded \(I(V)\) curves in Figure 2a, the SBH of the pristine region is approximately \((0.37 \pm 0.02)\) eV and the ideality factor is 1.1. The defected region shows a slightly higher current at the reverse bias (see Figure 2a). This is a result of a change in the SBH and ideality factor. The SBH for the defected region is \((0.24 \pm 0.04)\) eV with an ideality factor of 1.5. As the SBH is lower, more current can pass through the junction.

The advantage of using a sharp AFM tip as the metal electrode in the MSJ is the ability to record individual \(I(V)\) curves at every point of the surface. Figure 2b shows a spatially resolved current map extracted from a 128 \times 128 grid of individual \(I(V)\) curves at a bias voltage of \(-0.15\) V. A clear difference is found between the defects and pristine region, as already observed in the C-AFM image (see Figure 1b\(^8\)). We can now extract the SBH for each of the individual curves and construct a SBH map (Figure 2c). Significant inhomogeneities in the barrier height are observed. Interestingly, the SBH remains constant on the pristine regions of the MoSe\(_2\) surface, whereas directly above the defects, a decrease of the barrier height is measured.

The histogram in Figure 2d is constructed of the current values within a specific part of the SBH map (marked with the dashed box in Figure 2c). It reveals three peaks: corresponding to the pristine region \(\left(\text{at } (0.37 \pm 0.03)\text{ eV}\right)\), the defected region \(\left((0.24 \pm 0.04)\text{ eV}\right)\), and a third peak at \((0.30 \pm 0.02)\) eV. A closer look at the current and SBH maps confirms the presence of defects located in the second trilayer, in line with the C-AFM images of Figure 1b. Recent calculations showed that the influence of defects on the SBH decreases as the dopant-interface distance increases.\(^{57}\) Therefore, defects in the second trilayer have a weaker influence on the SBH compared to defects in the first trilayer.

We have also observed defect-induced reduction of the SBH for WS\(_2\), WSe\(_2\), MoTe\(_2\) (see the Supporting Information), and MoSe\(_2\).\(^{20}\) However, the absolute values of the SBH on the pristine and defected regions differ between the different TMDCs (using the same tip). This is a result of the different electron affinities and electronegativities of the various TMDC semiconductors. According to the Schottky–Mott rule (see eq 1), the SBH decreases linearly with increasing electron affinity. Although a decreasing trend is found, it is not linear and the experimentally found SBH values do not match with the prediction of the Schottky–Mott rule.

**Metal-Induced Gap States.** The discrepancy between the predicted and measured SBHs has also been found in other studies for conventional as well as layered semiconductors.\(^{6,19,24,58-60}\) The Schottky–Mott rule assumes that there is no charge transfer between the metal and the interface states of the semiconductor. However, other studies suggested that charge transfer should also be included for the metal/two-dimensional (2D) material MSJ.\(^{21,60}\) Generally, FLP is characterized using two different methods: (1) the Schottky–Mott approach and (2) the electronegativity concept. In the case of the Schottky–Mott approach, the SBH is given by

\[
\phi_B = S(\phi_M - \phi_{CNL}) + (\phi_{CNL} - \chi) \tag{6}
\]

where \(S\) is the Schottky pinning parameter \((S = d\phi_B/d\phi_M)\), \(\chi\) is the electron affinity of the semiconductor, and \(\phi_{CNL}\) is the charge neutrality level with respect to the vacuum level which is given by

\[
\phi_{CNL} = \frac{\chi + b}{1 - S} \tag{7}
\]

where \(b\) is the \(y\)-intercept of the \(\phi_B\) versus \(\phi_M\) graph. \(S\) is dependent on the density of interface states per unit area \(N\) and their extend into the semiconductor \(\delta\) as

\[
S = \frac{1}{1 + \frac{\varepsilon'_{\delta}}{r_{\phi}S}} \tag{8}
\]

with \(\varepsilon'_{\delta}\) being the absolute permittivity of the interface. When \(S \approx 1\), the Schottky–Mott limit is recovered (no pinning, \(N \approx 0\), no gap states) and the SBH is given by eq 1, whereas for \(S = 0\), the SBH is described by the Bardeen limit of strong pinning. In the Bardeen limit, the metal Fermi level is pinned by the interface states at \(\phi_{CNL}\).

In the electronegativity concept, the SBH is determined using...
converted to 4.9 eV, both the defects (0.14 ± 0.03) eV. The Schottky barrier is lower on both the pristine and defected regions as compared to the measurements obtained with the Pt tip (Figure 2c). The Schottky barrier is lower on both the pristine and defected regions as compared to the measurements obtained with the Pt tip (Figure 2c). The Schottky barrier is lower on both the pristine and defected regions as compared to the measurements obtained with the Pt tip (Figure 2c). (b) Extracted SBH map (200 × 200 nm², the scale bar is 50 nm) for MoTe₂ with a Pt tip (ϕₚ = 5.64). The SBH is lower as compared to MoSe₂ (Figure 2c) because of the different electron affinities (X_MoSe₂ > X_MoTe₂) and electronegativities (X_MoSe₂ > X_MoTe₂). (c,d) SBH for the pristine regions as a function of (c) metal (tip) work function (ϕₚ) and (d) electronegativity difference (X_M - X_TMDc) for the various TMDCs. The pinning factors are extracted using eqs 6 and 9.

\[ \phi_B = \phi'_\text{CNL} + S(X_M - X_{\text{TMDc}}) \]  

with \( S \) the experimentally obtained pinning factor (\( S = d\phi_B/ \) d\( X \)), \( X_M \) the electronegativity of the metal, \( X_{\text{TMDc}} \) the electronegativity of the TMDc, and \( \phi'_\text{CNL} \) the charge neutrality level with respect to the vacuum level. The difference between the concepts is the use of a surface property (work function and electron affinity) for the Schottky–Mott concept and a bulk property (electronegativity) for the electronegativity concept.

In order to determine the pinning factors and charge neutrality levels of the different TMDCs, the dependence of the \( \phi_B \) on the tip work function and electronegativity should be systematically studied. Therefore, we have performed the same measurements with two additional AFM tips: a PtSi tip (\( \phi_{\text{PtSi}} \approx 4.9 \text{ eV}, X_{\text{PtSi}} \approx 2.08 \text{, contact area 5.7 nm}^2 \)) and a highly n-doped Si tip (\( \phi_{\text{Si}} \approx 4.15 \text{ eV}, X_{\text{Si}} \approx 1.9 \text{, contact area 1.5 nm}^2 \)). For both tips, similar maps are obtained as for the Pt tip. Figure 3a shows the extracted SBH map for a PtSi tip on MoSe₂. A decrease of approximately 33% in the SBH is observed compared to the results obtained with the Pt tip on MoSe₂ for both the defects [(0.14 ± 0.03) eV] and the pristine region [(0.24 ± 0.02) eV]. This is attributed to the lower work function and electronegativity of the PtSi tip. In addition, defects in the second trilayer are no longer observed. The absolute value of the SBH decreases (as well as the absolute difference) making it no longer possible to resolve the presence of defects in the second trilayer.

Measurements performed with a Pt tip on MoTe₂ (Figure 3b) reveal a lower SBH as compared to the same measurements on MoSe₂ (Figure 2c). The distinct difference between the SBHs is in line with the different electron affinities and electronegativities of MoSe₂ and MoTe₂ where \( X_{\text{MoSe₂}} > X_{\text{MoTe₂}} \) and \( X_{\text{MoSe₂}} > X_{\text{MoTe₂}} \). According to the Schottky–Mott rule (eq 1), the MoTe₂ should have a lower SBH. However, the absolute change in the SBHs cannot be explained using the Schottky–Mott rule, as charge transfer is not included in the model.

To explain the discrepancy between the obtained SBH values and the Schottky–Mott rule, the pinning factors and charge neutrality levels of the studied TMDCs have to be included. Figure 3c plots the experimentally obtained SBHs for the pristine region of the studied TMDCs versus the metal

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**Table 1. Pinning Factors for Both the Pristine and Defected Regions for Different TMDCs**

| TMDC    | \( S_{\text{pristine}} \) | \( S_{\text{pristine}} \rightarrow S_{\text{pristine}} \) | \( S_{\text{defect}} \) | \( S_{\text{defect}} \rightarrow S_{\text{defect}} \) |
|---------|--------------------------|-----------------------------|-------------------|-------------------|
| MoSe₂   | 0.30 ± 0.03              | 0.65 ± 0.07                 | 0.28 ± 0.03       | 0.11 ± 0.02       |
| MoSe₁   | 0.19 ± 0.03              | 0.38 ± 0.04                 | 0.17 ± 0.02       | 0.11 ± 0.02       |
| MoTe₁   | 0.11 ± 0.02              | 0.21 ± 0.03                 | 0.10 ± 0.02       | 0.04 ± 0.01       |
| WS₂     | 0.21 ± 0.03              | 0.42 ± 0.06                 | 0.19 ± 0.03       | 0.08 ± 0.01       |
| WS₁     | 0.28 ± 0.03              | 0.61 ± 0.07                 | 0.27 ± 0.03       | 0.09 ± 0.02       |
| WS₁     | 0.28 ± 0.03              | 0.61 ± 0.07                 | 0.27 ± 0.03       | 0.09 ± 0.02       |

*The pinning factors are obtained via two different concepts: (1) Schottky–Mott relation (S) and (2) electronegativity concept (S'). S' is converted to S (S' \( \rightarrow S \)) using the relation S' = 2.275S.² The pinning factors are extracted from Figures 3c,d and S4b.
work function of the used tips. The SBHs for all of the TMDCs depend linearly on the work function of the metal, despite the different interactions between the TMDCs and the various tips. In all four cases (see Table 1), a strong FLP is observed, implying a strong interaction between the metal contact and the TMDC. The observed pinning factor of the pristine surface of WS\(_2\) (S = 0.28) and MoTe\(_2\) (S = 0.11) is in good agreement with the theoretically predicted pinning factors.\(^{17}\)

The SBHs for MoSe\(_2\) (S = 0.19) and WS\(_2\) (S = 0.21) are slightly lower as compared to theory but still agree reasonably well.\(^{17}\) The small deviation may be a result of the doping level. In our study, all of the TMDCs are n-type doped (see the Supporting Information), whereas for many calculations, p-type-doped TMDCs are used.\(^{17}\) The different pinning factor values emphasize that a different degree of pinning occurs for different TMDCs, which from eq 8 implies that a different density of gap states is causing the FLP in each case (the penetration depth \(\delta\) is approximately constant for all of the TMDCs).\(^{17,59,60}\)

The linear dependence of the SBH as a function of the metal work function (Figure 3c) shows that an electric-dipole layer exists at the TMDC-Schottky contacts.\(^{21,66}\) Together with the strong FLP between the metal and the TMDC, it is suggested that the band-structure line up at the Schottky contact is determined by the same mechanism as for conventional semiconductors, which is described by the MIGS model. Within the MIGS model, the main origin of the gap states, which causes the pinning, is the evanescent states of the metal plane waves as they decay in the semiconductor band gap. Later, Gong et al.\(^{21}\) refined the exact pinning mechanism for TMDCs. They claimed that two interface effects induce FLP: first, the dipole formation is altering the work function and second, interface interactions weaken the transition-metal/chalcogen bonding, which introduces the formation of gap states.

To explore the effect of dipole formation in more detail, the SBH is plotted as a function of the respective electronegativity (\(X\)) difference between the metal and the semiconductor (see Figure 3d). A linear trend is observed in agreement with Figure 3c. The extracted pinning factors \(S\) are consistent with the pinning factors in Table 1. The obtained charge neutrality levels for all four TMDCs are located in proximity of the conduction band (see Table 2), which is expected for n-type Schottky barriers. The charge neutrality levels for the electronegativity concept do not match with the charge neutrality levels obtained using eq 7, but are comparable to previously found charge neutrality levels for other layered semiconductor compounds.\(^{65}\)

The difference between the two concepts is attributed to the use of surface (work function and electron affinity) and bulk properties (electronegativities). The preference for using the electronegativity rather than the work function for calculating the charge neutrality level was led by the difference between the internal work function related to the electronegativity and the measured work function due to the additional electronic contribution from the surface dipole of the metal.\(^{60,66,67}\)

When the electronegativities of both the metal and the semiconductor are equal, no charge transfer is expected to occur at the interface. The linear dependence observed between the SBH and the electronegativity difference demonstrates that dipoles indeed exist within metal/TMDC interfaces and follow the same trend as conventional semiconductors.\(^{66}\) In most cases, the semiconductor is more electronegative than the metal resulting in an electron accumulation on the TMDC side and depletion on the metal side of the interface. In other words, charge transfer from the metal toward the more electronegative TMDC occurs, increasing the work function of the metal in agreement with refs 21 and 68. Only for the case of a metal tip on MoTe\(_2\), the dipole moment switches, reducing the work function of the metal.

Further evidence that TMDC-based MSJs follow the MIGS model is presented in Figure 4, where the experimentally obtained inverse pinning factor is plotted versus the optical part of the dielectric constant, \(\varepsilon_{\infty}\). In 1978, Schlüter proposed that there is a relation between the SBH of conventional semiconductors and their dielectric constant.\(^{66}\) Later, Tersoff\(^{69}\) suggested a correlation with the optical dielectric constant, \(\varepsilon_{\infty}\), which was later extended by Mönch,\(^{70}\) who found that \(S\) obeys the empirical relation

\[
S \propto \frac{1}{1 + 0.1(\varepsilon_{\infty} - 1)^2}
\]
The solid lines in Figure 4 clearly show that all types of semiconductors (including TMDCs) follow the relation given in eq 10 and that FLP in TMDCs can be described by the MIGS model.17 The vertical shift of the TMDC data (□ in Figure 4) with respect to the conventional semiconductors (△ in Figure 4) to lower pinning factors is caused by a lower net density of gap states (N) in eq 8. Using eq 8, the density of gap states can be estimated. Assuming that the penetration depth is δ ≈ 2 Å59 and ε ≈ 773 (note here: this is not ε∞) for the various TMDCs (except MoTe2), the density of gap states N is estimated at 1 × 1014 states/eV cm2. The obtained density is lower than the theoretically calculated value 2.3 × 1014 states/eV cm2 for a jellium/diamond interface67,74 (in good agreement with Figure 4, where S_{diamond} < S_{TMDC}). From Figure 4, the low pinning factor for MoTe2 with respect to the other TMDCs is also explained. The number of MIGS is inversely dependent on the width of the optical band gap.61 As MoTe2 has a smaller optical band gap than the other TMDCs, more MIGS are present in the Schottky junction and a stronger FLP is observed.

Furthermore, it was suggested that the presence of defects gives rise to extra pinning because of DIGS.10,17,24,75 Figure 5a,b shows the SBH for the defected regions of the TMDCs as a function of the metal work function and the electronegativity difference, respectively. Tables 1 and 2 give an overview of the extracted pinning factor and charge neutrality levels. In the investigated cases, the FLP is stronger at the positions of the defects. In the majority of the cases, a drop of approximately 30−40% in the pinning factor is observed for defected regions with respect to the pristine surface. This is the result of DIGS. Defects lead to the formation of dangling bonds, which result in variations of the transition-metal orbital symmetry.26 Consequently, some empty states become occupied and move into the band gap to form DIGS.76,77 The effect of the defects on the SBH, pinning factor, and charge neutrality level is independent of the TMDC type (complimentary with the observation in the current image of the C-AFM and in the STM), implying that the defects are of the same origin. As already mentioned earlier, these defects are most probably transition-metal vacancies or substitutional defects.29,36,37

Several experimental10,24 and theoretical studies17,26,38 also observed an increase in FLP because of defects. In these studies, chalcogen vacancies were assigned as the origin of the DIGS. Similar to MoS2,30 the strong FLP in this study is not caused by chalcogen vacancies as these are (1) still present on the pristine surface, (2) do not influence the conductivity, and (3) do not significantly alter their surroundings within the C-AFM and STM images (see Figure 1c). In addition, the pinning factors of the pristine regions (including chalcogen defects) are in good agreement with theory. In contrast, the pinning factor of the defected regions (induced by transition-metal vacancies or substitutional defects) corresponds well to the pinning factors found in previously reported experimental studies.19,20

When the pinning factors of the defected regions for the various TMDCs are plotted as a function of the optical dielectric constant (□ in Figure 4), the same trend is observed for the pristine regions. The points are shifted to lower pinning factors as the DIGS increase the net density of gap states (N). The defected TMDC curve coincides with the curve for conventional semiconductors, implying that the net density of gap states (N) is similar.

Unfortunately, FLP still occurs when MSJs are constructed using a conventional metal and TMDCs as a semiconductor, on contrary to the expectations based on their weak bonding with other materials. Several studies proposed promising paths to reduce FLP in TMDCs, such as the use of buffer layers25 or the use of other van der Waals materials as the contact material.78,79 Even in these junctions, subsurface defects will lower the SBH and will have a tremendous impact on the device performance. Furthermore, the effect of defects will be more pronounced when electronics are scaled down, wherein the contact area is just a few nanometers. Therefore, the conductance variations induced by transition-metal vacancies (or substitutional) should be considered in device characterization and predictability.

CONCLUSIONS

In summary, using C-AFM and STM, we have studied the underlying mechanisms behind FLP in various TMDCs. Using a nanoscopic MSJ, we were able to distinguish between intrinsic and extrinsic factors responsible for the FLP. Spatially resolved SBH maps reveal a substantial difference between pristine and defected regions of the TMDC surface depending
on the work function of the metal AFM tip. A strong FLP was observed on the pristine regions which can be explained by the MIGS model in line with conventional semiconductors. The extracted pinning factors are in good agreement with the theoretically predicted values. The defects induce an even stronger FLP (30–40%) because of DIGS. The pinning factor found in defected regions agrees well with the experimental values obtained in previous studies where large metal contacts were used. Our findings show that on van der Waals semiconductor surfaces without dangling bonds, the Fermi level is still heavily pinned because of MIGS. Moreover, the FLP is enhanced in the surroundings of subsurface defects because of DIGS. These defects can provide an alternative route for surface functionalization for device applications.

## METHODS

The TMDCs were mechanically cleaved and subsequently inserted in the AFM environmental chamber. The measurements were performed in N₂ environment by continuously purging with N₂ gas in order to reduce the influence from contaminants. The samples were imaged in the contact mode with an Agilent S1000 AFM using conductive probes. For the C-AFM measurements, the tip was grounded, whereas a bias voltage was applied to the various TMDC crystals. The AFM measurements, the tip was grounded, whereas a bias voltage was applied to the various TMDC crystals. The TMDCs were mechanically cleaved and subsequently inserted in the AFM environmental chamber. The measurements were performed in N₂ environment by continuously purging with N₂ gas in order to reduce the influence from contaminants. The samples were imaged in the contact mode with an Agilent S1000 AFM using conductive probes. For the C-AFM measurements, the tip was grounded, whereas a bias voltage was applied to the various TMDC crystals. The TMDCs were mechanically cleaved and subsequently inserted in the AFM environmental chamber. The measurements were performed in N₂ environment by continuously purging with N₂ gas in order to reduce the influence from contaminants. The samples were imaged in the contact mode with an Agilent S1000 AFM using conductive probes.

## ASSOCIATED CONTENT

Supporting Information

Experimental configuration, cantilever and material properties, defect types, ideality factor, MoSe₂, MoTe₂, WS₂, WSe₂, and pinning factor versus optical dielectric constant (PDF)

## AUTHOR INFORMATION

Corresponding Authors

*E-mail: k.sotthewes@utwente.nl (K.S.).
*E-mail: bampoulis@ph2.uni-koeln.de (P.B.).

ORCID

Kai Sotthewes: 0000-0003-2073-6958
Edwin Dollekmamp: 0000-0001-8956-5785
Pantelis Bampoulis: 0000-0002-2347-5223

Present Address

§II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany.

Notes

The authors declare no competing financial interest.

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## ADDITIONAL NOTE

“The defects are displayed elongated because of drift in the AFM.

## REFERENCES

1. Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. Nat. Nanotechnol. 2012, 7, 699.
2. Duan, X.; Wang, C.; Pan, A.; Yu, R.; Duan, X. Two-Dimensional Transition Metal Dichalcogenides as Atomically Thin Semiconductors: Opportunities and Challenges. Chem. Soc. Rev. 2015, 44, 8859–8876.
3. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Gallí, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. Nano Lett. 2010, 10, 1271–1275.
4. He, J.; Hummer, K.; Franchini, C. Stacking effects on the electronic and optical properties of bilayer transition metal dichalcogenides MoS₂, MoSe₂, WS₂, and WSe₂. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 89, 075409.
5. Kutana, A.; Penev, E. S.; Yakobson, B. I. Engineering Electronic Properties of Layered Transition-Metal Dichalcogenide Compounds Through Alloying. Nanoscale 2014, 6, 5820–5825.
6. Bampoulis, P.; Sotthewes, K.; Siekman, M. H.; Zandvliet, H. J. W. Local Conduction in MoW₁₋ₓSe₂: The Role of Stacking Faults, Defects, and Alloying. ACS Appl. Mater. Interfaces 2018, 10, 13218–13225.
7. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. Nat. Nanotechnol. 2011, 6, 147.
8. Kim, S.; Konar, A.; Hwang, W.-S.; Lee, J. H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.-B.; Choi, J.-Y.; et al. High-Mobility and Low-Power Thin-Film Transistors Based on Multilayer MoS₂ crystals. Nat. Commun. 2012, 3, 1011.
9. Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akincwande, D.; Lee, Y. H. Recent Development of Two-Dimensional Transition Metal Dichalcogenides and Their Applications. Mater. Today 2017, 20, 116–130.
10. Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multi-layer MoS₂ Transistors with Scandum Contacts. Nano Lett. 2012, 13, 100.
11. Pradhan, N. R.; Rhodes, D.; Zhang, Q.; Talapratra, S.; Terrones, M.; Ajayan, P. M.; Balicas, L. Intrinsic Carrier Mobility of Multilayered MoS₂ Field-Effect Transistors on SiO₂. Appl. Phys. Lett. 2013, 102, 123105.
12. Bernardi, M.; Palummo, M.; Grossman, J. C. Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials. Nano Lett. 2013, 13, 3664–3672.
13. Allain, A.; Kang, J.; Banerjee, K.; Kis, A. Electrical Contacts to Two-Dimensional Semiconductors. Nat. Mater. 2015, 14, 1195.
14. Schulman, D. S.; Arnold, A. J.; Das, S. Contact Engineering for 2D Materials and Devices. Chem. Soc. Rev. 2018, 47, 3037–3058.
15. Lince, J. R.; Carré, D. J.; Fleischauer, P. D. Schotky-Barrier Formation on a Covalent Semiconductor without Fermi-Level Pinning: The Metal-MoS₂(0001) Interface. Phys. Rev. B: Condens. Matter Mater. Phys. 1997, 56, 1647–1656.
16. Jaegermann, W.; Ohuchi, F. S.; Parkinson, B. A. Interaction of Cu, Ag and Au with van der Waals faces of WS₂, and SnS2. Surf. Sci. 1988, 201, 211–227.
17. Guo, Y.; Liu, D.; Robertson, J. 3D Behavior of Schottky Barriers of 2D Transition-Metal Dichalcogenides. ACS Appl. Mater. Interfaces 2015, 7, 25709.
18. Yuan, H.; Cheng, G.; You, L.; Li, H.; Zhu, H.; Li, W.; Kopanski, J. J.; Obeng, Y. S.; Walker, A. R. H.; Gundlach, D. J.; et al. Influence of
Metal-MoS2 Interface on MoS2 Transistor Performance: Comparison of Ag and Ti Contacts. ACS Appl. Mater. Interfaces 2015, 7, 1180–1187.

(19) Kim, C.; Moon, I.; Lee, D.; Choi, M. S.; Ahmed, F.; Nam, S.; Cho, Y.; Shin, H.-J.; Park, S.; Yoo, W. J. Fermi Level Pinning at Electrical Metal Contacts of Monolayer Molybdenum Dichalcogenides. ACS Nano 2017, 11, 1588–1596.

(20) Bampoulis, P.; van Bremmen, R.; Yao, Q.; Poelsema, B.; Zandvliet, H. J. W.; Sotthewes, K. Defect Dominated Charge Transport and Fermi Level Pinning in MoS2/Metal Contacts. ACS Appl. Mater. Interfaces 2017, 9, 19279–19286.

(21) Gong, C.; Colombo, L.; Wallace, R. M.; Cho, K. The Unusual Mechanism of Partial Fermi Level Pinning at Metal - MoS2 Interfaces. Nano Lett. 2014, 14, 1714.

(22) Heine, V. Theory of Surface States. Phys. Rev. 1965, 138, A1689.

(23) Hasegawa, H.; Ohno, H. Unified Disorder Induced Gap State Model for Insulator-Semiconductor and Metal-Semiconductor Interfaces. J. Vac. Sci. Technol., B: Microelectron. Process. Phenom. 1986, 4, 1130–1138.

(24) McDonnell, S.; Addou, R.; Buie, C.; Wallace, R. M.; Hinkle, C. L. Defect-Dominated Dopant Contacting and Dopant Resistance in MoS2. ACS Nano 2014, 8, 2880.

(25) Kim, G.-S.; Kim, S.-H.; Park, J.; Han, K. H.; Kim, J.; Yu, H.-Y. Schottky Barrier Height Engineering for Electrical Contacts of Multilayered MoS2 Transistors with Reduction of Metal-Induced Gap States. ACS Nano 2018, 12, 6292–6300.

(26) Su, J.; Feng, L.; Zhang, Y.; Liu, Z. Defect Induced Gap States in Monolayer MoS2 Control the Schottky Barriers of Pt-mMoS2 Interfaces. Appl. Phys. Lett. 2017, 110, 161604.

(27) Hong, J.; Hu, Z.; Probert, M.; Li, K.; Lv, D.; Yang, X.; Gu, L.; Mao, N.; Feng, Q.; Xie, L.; et al. Exploring Atomic Defects in Molybdenum Disulphide Monolayers. Nat. Commun. 2015, 6, 6293.

(28) Addou, R.; Colombo, L.; Wallace, R. M. Surface Defects on Natural MoS2. ACS Appl. Mater. Interfaces 2015, 7, 11921–11929.

(29) Addou, R.; Wallace, R. M. Surface Analysis of WSe2 Crystals: Spatial and Electronic Variability. ACS Appl. Mater. Interfaces 2016, 8, 26400–26406.

(30) Fu, D.; Zhou, J.; Tongay, S.; Liu, K.; Fan, W.; King Liu, T.-J.; Wu, J. Mechanically Modulated Tunneling Resistance in Monolayer MoS2. Appl. Phys. Lett. 2013, 103, 183105.

(31) Giannazzo, F.; Fischella, G.; Piazza, A.; Agnello, S.; Roccaforte, F. Nano-scale Inhomogeneity of the Schottky Barrier and Resistivity in MoS2 Multilayers. Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 92, 081307.

(32) Giannazzo, F.; Fischella, G.; Piazza, A.; Di Franco, S.; Oliveri, I. P.; Agnello, S.; Roccaforte, F. Current injection from metal to MoS2 Probed at Nanoscale by Conductive Atomic Force Microscopy. Mater. Sci. Semicond. Process. 2016, 42, 174–178.

(33) Bampoulis, P.; Sotthewes, K.; Sekman, M. H.; Zandvliet, H. J. W.; Poelsema, B. Graphene Visualizes the Ion Distribution on Air-Cleaved Mica. Sci. Rep. 2017, 7, 43451.

(34) Giannazzo, F.; Fischella, G.; Greco, G.; Di Franco, S.; Deretzi, I.; La Magna, A.; Bongiorno, C.; Nicoira, G.; Spinella, C.; Scopelliti, M.; et al. Ambipolar MoS2 Transistors by Nanoscale Tailoring of Schottky Barrier Using Oxygen Plasma Functionalization. ACS Appl. Mater. Interfaces 2017, 9, 23164–23174.

(35) Sotthewes, K.; Bampoulis, P.; Zandvliet, H. J. W.; Lohse, D.; Poelsema, B. Pressure-Induced Melting of Confined Ice. ACS Nano 2017, 11, 12723–12731.

(36) Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Irobo, J.-C. Intrinsic Structural Defects in Monolayer Molybdenum Disulphide. Nat. Lett. 2013, 13, 2615.

(37) Ke, S.; Longo, R. C.; Addou, R.; Wallace, R. M.; Cho, K. Impact of Intrinsic Atomic Defects on the Electronic Structure of MoS2 Nanotubes. Nanotechnology 2014, 25, 375703.
(58) Mönch, W. Valence-Band Offsets and Schottky Barrier Heights of Layered Semiconductors Explained by Interface-Induced Gap States. Appl. Phys. Lett. 1998, 72, 1899–1901.
(59) Kang, J.; Liu, W.; Sarkar, D.; Jena, D.; Banerjee, K. Computational Study of Metal Contacts to Monolayer Transition-Metal Dichalcogenide Semiconductors. Phys. Rev. X 2014, 4, 031005.
(60) Mönch, W. Explanation of the Barrier Heights of Graphene Schottky Contacts by the MIGS-and-Electronegativity Concept. J. Appl. Phys. 2016, 120, 104501.
(61) Mönch, W. Chemical Trends of Barrier Heights in Metal-Semiconductor Contacts: On the Theory of the Slope Parameter. Appl. Surf. Sci. 1996, 92, 367–371.
(62) Robertson, J. Band offsets of wide-band-gap oxides and implications for future electronic devices. J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom. 2000, 18, 1785–1791.
(63) Rasmusen, F. A.; Thygesen, K. S. Computational 2D Materials Database: Electronic Structure of Transition-Metal Dichalcogenides and Oxides. J. Phys. Chem. C 2015, 119, 13169–13183.
(64) Guo, Y.; Robertson, J. Band engineering in transition metal dichalcogenides: Stacked versus lateral heterostructures. Appl. Phys. Lett. 2016, 108, 233104.
(65) Brudnyi, V. N.; Sarkisov, S. Y.; Kosobutsky, A. V. Electronic properties of GaSe, InSe, GaS and GaTe layered semiconductors: charge neutrality level and interface barrier heights. Semicond. Sci. Technol. 2015, 30, 115019.
(66) Schlüter, M. Chemical Trends in Metal-Semiconductor Barrier Heights. Phys. Rev. B: Condens. Matter Mater. Phys. 1978, 17, 5044–5047.
(67) Tsugawa, K.; Noda, H.; Hirose, K.; Kawarada, H. Schottky Barrier Heights, Carrier Density, and Negative Electron Affinity of Hydrogen-Terminated Diamond. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 81, 045303.
(68) Pan, Y.; Li, S.; Ye, M.; Qiuhe, R.; Song, Z.; Wang, Y.; Zheng, J.; Pan, F.; Guo, W.; Yang, J.; et al. Interfacial Properties of Monolayer MoSe2-Metal Contacts. J. Phys. Chem. C 2016, 120, 13063–13070.
(69) Tersoff, J. Calculation of Schottky Barrier Heights from Semiconductor Band Structures. Surf. Sci. 1986, 168, 275–284.
(70) Mönch, W. Metal-Semiconductor Contacts: Electronic Properties. Surf. Sci. 1994, 299-300, 928–944.
(71) Mönch, W. Role of Virtual Gap States and Defects in Metal-Semiconductor Contacts. Phys. Rev. Lett. 1987, 58, 1260–1263.
(72) Bell, M. G.; Liang, W. Y. Electron Energy Loss Studies in Solids: The Transition Metal Dichalcogenides. Adv. Phys. 1976, 25, 53–86.
(73) Laturia, A.; Van de Put, M. L.; Vandenbergh, W. G. Dielectric Properties of Hexagonal Boron Nitride and Transition Metal Dichalcogenides: from Monolayer to Bulk. npj 2D Mater. Appl. 2018, 2, 6.
(74) Ihm, J.; Louie, S. G.; Cohen, M. L. Diamond-Metal Interfaces and the Theory of Schottky Barriers. Phys. Rev. Lett. 1978, 40, 1208–1211.
(75) Han, Y.; Wu, Z.; Xu, S.; Chen, X.; Wang, L.; Wang, Y.; Xiong, W.; Han, T.; Ye, W.; Lin, J.; et al. Probing Defect-Induced Midgap States in MoS2 Through Graphene-MoS2 Heterostructures. Adv. Mater. Interfaces 2015, 2, 1500064.
(76) Qu, H.; Xu, T.; Wang, Z.; Ren, W.; Nan, H.; Ni, Z.; Chen, Q.; Yuan, S.; Miao, F.; Song, F.; et al. Hopping Transport Through Defect-Induced Localized States in Molybdenum Disulphide. Nat. Commun. 2013, 4, 2642.
(77) Feng, L.; Su, J. Effect of Vacancies on Structural, Electronic and Optical Properties of Monolayer MoS2: A First-Principles Study. J. Alloy. Comp. 2014, 613, 122–127.
(78) Liu, Y.; Stradins, P.; Wei, S.-H. Van der Waals Metal-Semiconductor Junction: Weak Fermi Level Pinning Enables Effective Tuning of Schottky Barrier. Sci. Adv. 2016, 2, No. e1600069.
(79) Chanana, A.; Mahapatra, S. Prospects of Zero Schottky Barrier Height in a Graphene-Inserted MoS2-Metal Interface. J. Appl. Phys. 2016, 119, 014303.