Two-dimensional ferromagnet/semiconductor transition metal dichalcogenide contacts: p-type Schottky barrier and spin-injection control

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We study the ferromagnet/semiconductor contacts formed by transition metal dichalcogenide monolayers, focusing on semiconducting MoS2 and WS2 and ferromagnetic VS2. We investigate the degree of p-type doping and demonstrate tuning of the Schottky barrier height by vertical compressive pressure. An analytical model is presented for the barrier heights that accurately describes the numerical findings and is expected to be of general validity for all transition metal dichalcogenide metal/semiconductor contacts. Furthermore, magnetic proximity effects induce a 100% spin polarization at the Fermi level in the semiconductor where the spin splitting increases up to 0.70 eV for increasing pressure.

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I. INTRODUCTION

Two-dimensional (2D) materials exhibit unique properties, which often are distinctly different from their bulk counterparts, thus having created tremendous interest in synthesis and application.1–3 In particular, the monolayers of semiconducting transition metal dichalcogenides (TMDCs), such as MoS2 and WS2, exhibit versatile electronic4–8 and optical,9–12 mechanical,13–15 and chemical16–18 properties, offering opportunities beyond the more famous graphene and therefore opening up new fundamental as well as technological avenues for inorganic 2D materials in a range of fields, including electronic devices, catalysis, and energy storage.19

Semiconductor-to-metal transitions have been predicted for TMDC bilayers in external electric fields20 and under vertical compressive pressure.21 In order to tune the electronic properties of semiconducting 2D TMDCs, hybrid systems have been put forward. Radisavljevic and co-workers22 have reported on few-layer 2D TMDC integrated electronic circuits that are able to perform digital logic operations. The MoS2/graphene hybrid system has been reported to show a high electron conductivity and excellent electrochemical and thermoelectric performances.23–26 Therefore, combining TMDCs with other 2D layered materials is a viable and promising way to realize vertical heterostructures and hybrid all-2D devices.27,28

Metal/semiconductor contacts play a key role in modern electronic and photonic devices, since the created Schottky barriers dominate the transport behavior.29 It has been found that the barrier height in MoS2 drastically depends on the electrodes.30 More recently, a back gate voltage has been applied to manipulate the barrier height in MoS2 field effective transistors contacted with cobalt electrodes.31 In addition, for potential spintronics applications, understanding the contacts with ferromagnetic substrates is crucial to realize efficient spin injection and enhance the spin polarization of the current across the interface.32,33

Introduction of transition metal atoms34 and contacting with ferromagnetic substrates35 have been reported to yield spin injection and spin transport in monolayer MoS2. 2D TMDCs constitute a large family of materials and possess the advantage that the electronic properties range from ferromagnets (such as VS2 and NbS2)36–38 to semiconductors,39 opening the possibility of ferromagnet/semiconductor contacts for engineering all-2D electronic devices and for realizing spin polarization.28 In this context, we propose a class of ferromagnet/semiconductor contacts completely based on TMDC monolayers.

In the following, we investigate Schottky contacts in 2D TMDCs, focusing on the nonmagnetic semiconductors MoS2 and WS2 and the ferromagnet VS2 as prototypes. We will argue that the degree of p-type doping and the corresponding Schottky barrier heights in MoS2 and WS2 can be controlled by vertical compressive pressure. A comprehensive picture is derived to understand the mechanism of the pressure dependence. We will also argue that magnetic proximity effects30–42 induce 100% spin polarization in MoS2 and WS2 at the Fermi level (EF) in a wide pressure range. These findings pave the way for designing coherent dopant-free all-2D contacts for future spin transport applications.

II. COMPUTATIONAL METHODS

First-principles calculations are performed using the Vienna Ab Initio Simulation Package with the spin polarized Perdew, Burke, and Ernzerhof generalized gradient approximation functional. In each case we apply a vacuum slab of at least 29 Å thickness. A cutoff energy of 500 eV and a Γ-centered 30 × 30 × 1 k-mesh are used. The geometry is optimized until all residual forces are less than 0.01 eV/Å. Because of the absence of strong bonding a damped van der Waals correction,43,44 which is a significant improvement with respect to the generalized gradient approximation (though dipole-dipole corrections are limited in precision), is adapted to model nonbonding forces. We note that the Schottky barrier is an intrinsic property of the interface and defined by the relative alignment of EF of the metal and the valence-band maximum (VBM, p-type barrier height φB,p) or conduction-band minimum (CBM, n-type barrier height φB,n) of the semiconductor.

III. RESULTS AND DISCUSSION

VS2 monolayers exist in two polymorphs, trigonal prismatic (hVS2) and octahedral (tVS2), with D3h and D3d point groups, respectively.39 Monolayer VS2 has the former structure at and below room temperature.35 The properties obtained in our calculations for the two phases are
summarized in Table I. The former is 27 meV more stable, with the energy difference between spin degeneracy and polarization four times that of the latter. The in-plane lattice constants are the same, whereas the V-S bonds are slightly longer in hV S₂. The calculated band structures, see Fig. 1, indicate that both phases are metallic with magnetic moments of 1.00 μB and 0.48 μB per unit cell. In hV S₂ the magnetic moments of V and S are 1.02 and −0.05 μB, respectively, while the corresponding values in rV S₂ are 0.51 and −0.03 μB. The calculated work function of hV S₂ is 0.46 eV larger than that of rV S₂. All these results agree well with previous experimental and theoretical studies.35,37,46

The relaxed lattice constant of both MoS₂ and WS₂ is 3.181 Å, i.e., the lattice mismatch to VS₂ is tiny (∼0.2%). Thus, the average value of 3.177 Å is adopted for all the hybrid systems. For the contact with trigonal prismatic hV S₂ two stacking modes are considered, namely AA and AB, in which the Mo or W atoms are on top of V and S, respectively. Correspondingly, the interfaces are labeled hV S₂/MoS₂-AA, hV S₂/MoS₂-AB, hV S₂/WS₂-AA, and hV S₂/WS₂-AB. For the contact with octahedral rV S₂ there are in total six configurations: The atop-I and II patterns have S above S(1) and Mo or W above V and S(2), respectively, the hcp-I and II patterns have S above V and Mo or W above S(1) and S(2), and the fcc-I and II patterns have S above S(2) and Mo or W above S(1) and V. The structures of the hV S₂/MoS₂ and hV S₂/WS₂ interfaces are shown in Fig. 2(d). The binding energy of an interface is defined as EM = EIS − EM − EV, where EIS, EM, and EV represent the total energies of the hybrid system, MoS₂ or WS₂, and VS₂, respectively. The obtained binding energies per interface metal atom as a function of the interface separation D between MoS₂ or WS₂ and VS₂ are shown in Figs. 2(a)–2(c).

![Figure 1](image.png)

**Figure 1.** (Color online) Spin polarized band structures of (a) hV S₂ and (b) rV S₂. Red and blue lines correspond to the spin majority and minority bands, respectively.

We first focus on the bilayer systems with MoS₂ or WS₂ on VS₂ in the trigonal prismatic phase. As is shown in Figs. 2(a) and 2(b), the interaction between MoS₂ or WS₂ and VS₂ is similar to that in MoS₂/Ti₃C₂ and hV S₂/WS₂. The equilibrium positions are the same in the two systems, 3.7 and 3.1 Å in the AA and AB stackings, respectively. For a separation larger than ∼3.9 Å the AA and AB energy profiles overlap, indicating that the cases are degenerate with the interface formation still being exothermic. Figure 3 shows densities of states of MoS₂, WS₂, and VS₂ in hV S₂/MoS₂-AA and hV S₂/WS₂-AA at D = 2.4 Å and at the equilibrium positions to explore the electronic structure variations in the semiconductors upon the interface formation. It can be seen that the interface interaction modifies the electronic properties remarkably. At D = 2.4 Å the electronic properties show a strong hybridization and the band gap is narrowed by 0.49 eV. The effective S-S distance is much smaller in the AA stacking, a lower pressure threshold has been found for the semiconductor-to-metal transition in Ref. 21. It can be expected that similar metallic features in MoS₂ and WS₂ can be obtained in the AB stacking at high enough pressure. At the respective equilibrium positions in hV S₂/MoS₂-AA and hV S₂/WS₂-AA the density of states shows that both MoS₂ and WS₂ preserve their semiconducting characters with slightly smaller band gaps of 73 and 41 meV respectively. Moreover, it can be seen from Figs. 3(b) and 3(d) that EF is close to the VBM, indicating a strong p-type doping with barrier heights of 0.26 and 0.20 eV.

According to Figs. 2(a) and 2(b), it is much more likely to have AB stacking in hV S₂/MoS₂ and hV S₂/WS₂ interfaces for a separation less than 3.1 Å. Electronic band structures for AB stacking at D = 2.4 Å and at the equilibrium positions are given in Figs. 4(a) and 4(b). Due to the similarity between hV S₂/MoS₂-AB and hV S₂/WS₂-AB we only show the former case. At D = 2.4 Å the MoS₂ VBM at the K point is lifted higher than that at the K point due to the typical interface interaction,21 and the band gap is narrowed by 0.49 eV. Additionally, the VBM at the Γ point shows an evident spin splitting of 0.34 eV with one spin channel even crossing EF, suggesting a shallow p-type doping. In the case of the equilibrium separation the VBM is still located at the Γ point, while the band-gap reduction (0.16 eV) and spin splitting (0.11 eV) are less pronounced. The VBM in both spin channels is located below EF, giving rise to a p-type Schottky barrier of 0.20 eV. The trend of the band-gap variation and Γ point spin splitting for D = 2.4 to 3.1 Å in Fig. 4(d) shows that hV S₂/MoS₂-AB and hV S₂/WS₂-AB behave similarly: When the separation decreases the band gap decreases and the spin splitting increases monotonously. It can be deduced that further reduction of the interface separation will result in shallower

| TABLE I. Total energy (Etot, normalized), energy difference (∆E) between spin degeneracy and polarization, in-plane lattice constant (a), V-S bond length (dV-S), layer thickness (dS-S), magnetic moment (M), and work function (Φ) in the trigonal prismatic (hV S₂) and octahedral (rV S₂) phases. |
|---|---|---|---|---|---|
| Etot (meV) | ∆E (meV) | a (Å) | dV-S (Å) | dS-S (Å) | M (μB) | Φ (eV) |
| hV S₂ | 48 | 3.174 | 2.362 | 2.981 | 1.00 | 5.87 |
| rV S₂ | 27 | 3.174 | 2.349 | 2.940 | 0.48 | 5.41 |

**FIG. 1.** (Color online) Spin polarized band structures of (a) hV S₂ and (b) rV S₂. Red and blue lines correspond to the spin majority and minority bands, respectively.
FIG. 2. (Color online) Binding energy per interface metal atom as a function of the interface separation \( (D) \) in (a) \( hVS_2/MoS_2 \), (b) \( hVS_2/WS_2 \), and (c) \( rVS_2/MoS_2 \). The equilibrium positions are indicated by stars. (d) Side views of the nonequivalent configurations of \( hVS_2/MoS_2 \) and \( rVS_2/MoS_2 \). Yellow, gray, and red balls represent S, Mo, and V atoms, respectively.

\( p \)-type doping and in an enhanced spin splitting in the two semiconductors.

We turn to the interfaces with VS\(_2\) in the octahedral phase. As discussed above, MoS\(_2\) and WS\(_2\) in contact with \( hVS_2 \) show very similar results. Thus, we only consider the \( rVS_2/MoS_2 \) interface as an example. Figure 2(c) shows the binding energies as a function of the interface separation for the six configurations; see columns 2 to 4 in Fig. 2(d). According to the results, the six cases can be divided into two groups, similar to \( hVS_2/MoS_2 \): Arrangements with the S atom in MoS\(_2\) on top of S(1) in \( tVS_2 \), namely \( rVS_2/MoS_2\)-top-I and II, are less stable and belong to the AA stacking class, while the other four types are similar to the AB stacking and are more likely to form. Specifically, the four cases are almost degenerate, with fcc-II being slightly more stable, suggesting that all can be fabricated. The band structure of the fcc-II

FIG. 3. (Color online) Spin polarized partial density of states for VS\(_2\), MoS\(_2\), and WS\(_2\) in \( hVS_2/MoS_2\)-AA and \( hVS_2/WS_2\)-AA for (a), an interface separation of 2.4 Å and (b), the equilibrium position. In (b) and (d) the \( p \)-type Schottky barrier heights (\( \Phi_{\text{B},p} \)) are indicated.

FIG. 4. (Color online) Spin polarized band structures of \( hVS_2/MoS_2\)-AB for (a) \( D = 2.4 \) Å, (b) the equilibrium position, and (c) \( rVS_2/MoS_2\)-fcc-II at the equilibrium position. The MoS\(_2\) derived conduction and valence bands in the hybrid systems are indicated by white dotted curves. (d) Band-gap variation (black) and spin splitting at the \( \Gamma \) point (red) of MoS\(_2\) and WS\(_2\) as a function of the interface separation from \( D = 2.4 \) Å to the respective equilibrium position.
configuration at the equilibrium separation of $3.0 \text{ Å}$ is shown in Fig. 4(c) to investigate the electronic structure variations of MoS$_2$ in contact with VS$_2$. The VBM of MoS$_2$ is located at the $\Gamma$ point with the band gap narrowed by 0.18 eV and displays spin splitting. Moreover, $E_F$ is located only 0.16 eV below the midgap (CBM+VBM)/2, suggesting rather weak $p$-type doping. The corresponding Schottky barrier height is calculated to be 0.60 eV. Figure 4(d) shows as a function of the interface separation the MoS$_2$ band-gap variation and VBM spin splitting in $h$VS$_2$/MoS$_2$-fcc-II. Similar to the trends in $h$VS$_2$/MoS$_2$-AB, the band gap increases and the spin splitting decreases monotonously as the separation increases, with the band-gap changes being comparable in $h$VS$_2$/MoS$_2$ and $h$VS$_2$/WS$_2$. However, a much smaller spin splitting is found in $r$VS$_2$/MoS$_2$-fcc-II due to the smaller magnetic moment of VS$_2$.

It has been demonstrated above that different Schottky barrier heights are obtained by adjusting the interface separation in contact with both VS$_2$ and VS$_2$. In order to access the controllability of the barrier height in the experiment, the interface separations are next converted into vertical compressive pressures ($P$), which are calculated from the energy cost per unit area for reducing the separation,

$$P = \frac{E - E_0}{(D_0 - D)\lambda} \tag{1}$$

where $E$ and $E_0$ are the total energies at interface separations of $D$ and $D_0$ (equilibrium), and $\lambda$ is the area of the cell. Note that the pressure induced volume change is essentially due to the interface spacing, while only tiny shifts of the atomic positions are observed. The obtained barrier height as a function of $P$ in $h$VS$_2$/MoS$_2$-AB (circles) and $r$VS$_2$/MoS$_2$-fcc-II (squares) is displayed in Fig. 6(b). At $P = 4.3$ ($D = 2.5 \text{ Å}$) and 5.5 GPa ($D = 2.4 \text{ Å}$) the VBM of MoS$_2$ at the $\Gamma$ point is higher than $E_F$ in $h$VS$_2$/MoS$_2$-AB [see Fig. 4(a)]. Thus, the Schottky barrier height is extended into the “negative” region for comparison. Obviously, a similar trend is found in the two systems: $\Phi_{B,p}$ decreases monotonously with increasing $P$. Also, the changes are reversible, i.e., the structures relax back to the equilibrium with larger $\Phi_{B,p}$ in the absence of pressure, making the systems potentially applicable in sensors. Pressure dependent $p$-type Schottky barrier heights, from another point of view, also constitute an effective strategy to control the degree of $p$-type doping in semiconducting TMDC monolayers. The present $p$-type doping together with the $n$-type doping found in MoS$_2$ on transition metal substrates$^{30,31}$ opens access to $p$-$n$ junctions.

In order to better understand the metal-semiconductor junctions, we address the plane-averaged charge density difference $\Delta \rho(z)$ to visualize the charge redistribution at the interface. The case of $h$VS$_2$/MoS$_2$-AB at the equilibrium separation is shown in Fig. 5(a); similar plots are found for the other studied systems. It can be seen that electrons are transferred from the semiconductor side to the interface and the VS$_2$ side, consistent with the results of $p$-type doping in MoS$_2$. The induced charge transfer, which is estimated by integrating $\Delta \rho(z)$, amounts to 0.019 $|e|$. Particularly, a charge accumulation can be seen around the V layer, yielding a smaller local magnetic moment with respect to pristine $h$VS$_2$ (0.92 versus 1.02$\mu_B$). Figure 5(b) shows the separation dependent charge transfer and V magnetic moment. When the separation increases, both decrease gradually. This implies that the layer-layer interaction does not preclude charge transfer at the interface, similar to findings for MoS$_2$/Ti$_2$CY$_2$. However, the charge transfer here is the opposite direction, so that an integration of MoS$_2$/VS$_2$ and MoS$_2$/Ti$_2$CY$_2$ would give rise to a coherent dopant-free all-2D $p$-$n$ junction.$^{28,30}$

A schematic model is introduced in Fig. 6(a) to explain the effects on the $p$-type Schottky barrier height, which can be written as$^{51}$

$$\Phi_{B,p} = \Phi_{\text{MoS}_2} - \Phi_{\text{VS}_2} - \mu_{\text{IS}} \tag{2}$$

where $\Phi_{\text{MoS}_2}$ and $\Phi_{\text{VS}_2}$ are the electronic ionization potential of MoS$_2$ and the work function of VS$_2$, respectively. At the contact of MoS$_2$ and VS$_2$ an interface dipole $\mu_{\text{IS}}$ occurs as a result of charge rearrangements. Its sign is negative, since the charge is transferred away from the semiconductor side. Additionally, due to the interaction between $\Gamma$ point states,$^{49}$ the VMB of MoS$_2$ shifts upwards by $\Delta$ from its original position. Note that the semiconducting nature of MoS$_2$ (or WS$_2$) is preserved. The modification of the VS$_2$ work function is found to be tiny, i.e., $\Phi_{\text{VS}_2} \approx \Phi_{\text{VS}_2}^0$. As a consequence, Eq. (2) can be rewritten as

$$\Phi_{B,p} = (\mu_{\text{MoS}_2} - \Delta) - \Phi_{\text{VS}_2}^0 - \mu_{\text{IS}}$$

$$= (\mu_{\text{MoS}_2} - \Phi_{\text{VS}_2}^0) - \Delta - \mu_{\text{IS}} \tag{3}$$

where the superscript “0” denotes the pristine systems. Data obtained from Eq. (3) are shown by lines in Fig. 6(b) and reproduce the results of the band structure calculations very well. This fact suggests that three factors together determine the Schottky barrier height. The first is the intrinsic (and thus contact) difference between the electronic ionization potentials and work functions, respectively, of the pristine semiconductor and metal monolayers. The second is the MoS$_2$/VS$_2$ interface interaction, which leads to MoS$_2$ VBM upshifts. Note that, according to Ref. 47, even a large dipole shifts the energy levels only slightly. The last is the charge redistribution induced interface dipole. The interface barrier and MoS$_2$ VBM upshift as a function of the separation are shown in Figs. 6(c) and 6(d), respectively. It can be seen that the latter two factors are larger in $h$VS$_2$/MoS$_2$-AB, suggesting a stronger interaction and more pronounced charge transfer. The third factor depends less on $D$ due to its long-range nature. The ionization potential of...
pristine MoS$_2$ is 5.88 eV, giving the first contribution a value of 0.01 eV in $h$VS$_2$/MoS$_2$-AB. Accordingly, $\Phi_{B,p}$ is determined by the latter two contributions, where the second is larger than the third for pressure larger than 3.4 GPa, leading to negative barrier heights. In $t$VS$_2$/MoS$_2$ the first contribution (0.47 eV) is dominant and the latter two almost cancel out each other, thus resulting in higher barriers; see Fig. 6(b). By the similarity of this picture with TMDC/TMDC bilayers, the analytical model can be expected to be applicable to all TMDC metal/semiconductor contacts.

Understanding the spin injection into semiconducting 2D materials is important for spintronics applications. Figure 4(a) demonstrates 100% spin polarization in MoS$_2$ at $E_F$ with one spin channel crossing $E_F$ while the other stays below at $D = 2.4$ Å ($P = 5.5$ GPa) in $h$VS$_2$/MoS$_2$-AB. Similar results are obtained for $t$VS$_2$/MoS$_2$-AB. The results imply that it is feasible to achieve 100% spin polarization in an appropriate pressure range. According to Fig. 6(b), the minimum pressure for which the VBM at the $\Gamma$ point develops a spin splitting and one spin channel crosses $E_F$ is around 3.4 GPa. The maximum pressure at which the metallic feature becomes dominant in MoS$_2$, as is the case in $h$VS$_2$/MoS$_2$-AA for $D = 2.4$ Å [see Fig. 3(a)], is calculated to be around 18 GPa. Additionally, when the pressure increases from 3.4 to 18 GPa the spin splitting becomes larger and finally a value of 0.70 eV is obtained. However, in $t$VS$_2$/MoS$_2$, due to the large difference (0.47 eV) between the ionization potential of pristine MoS$_2$ and the work function of $t$VS$_2$, the two spin channels at the VBM of MoS$_2$ in the hybrid system hardly will shift above $E_F$, making it unlikely to have the same result as in $t$VS$_2$/MoS$_2$. Consequently, contacting MoS$_2$ with $h$VS$_2$ is a good strategy to realize an efficient spin injection for spintronics applications.

IV. CONCLUSIONS

We have discussed the results of first-principles calculations for the prototypical VS$_2$/MoS$_2$ and VS$_2$/WS$_2$ contacts to explore the physics of metal/semiconductor contacts constructed of TMDC monolayers. The degree of $p$-type doping as well as the Schottky barrier height in MoS$_2$ and WS$_2$ upon interface formation can be readily tuned by vertical compressive pressure. In addition, an analytical model has been introduced to understand which quantities determine the barrier height and to which degree. An almost ideal accuracy of the model suggests that three factors play the key role: the difference between the electronic ionization potential of the semiconductor and the work function of the metal, the VBM upshift, and the interface dipole. Moreover, similarity with the interaction in TMDC/TMDC bilayer systems indicates that the model is of general validity for TMDC metal/semiconductor contacts.

As a consequence of magnetic proximity effects, 100% spin polarization at $E_F$ is achieved in the MoS$_2$ layer in the pressure range from approximately 3.4 to 18 GPa. Within this range the spin splitting increases up to 0.70 eV. The obtained insights into 2D TMDC contacts are significant for designing all-2D metal/semiconductor contacts and also for further spin transport explorations.

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