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Simulation study of Fermi level depinning in metal-MoS₂ contacts

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Abstract

We used Density Functional Theory (DFT) to study the Fermi level pinning and Schottky barrier height in metal-MoS₂ contacts. We showed that the Fermi level de-pinning could be attained by controlling the distance between the metal and MoS₂. In particular, with proper buffer layers and the use of back-gated structures, the Schottky barrier height can be practically zeroed in some metal-MoS₂ stacks, which is important to attain Ohmic contacts.

1. Introduction and summary

Among 2D transition metal dichalcogenides, MoS₂ is the most technologically mature semiconductor [1]. Thanks to its extreme flexibility and large piezo-resistance [2], MoS₂ has great potentials for tactile sensing in soft robotics [3], for electronic skin [4] and fast thermal sensors [5], besides applications in nanoelectronic circuits [6]. But for most applications the quality of the metal-MoS₂ contact is critical, with best reported values being in the k Ω · μ m range [6], which sharply contrasts with the projections of the IRDS roadmap [7], targeting tens of Ω · μ m for nanoscale FETs.

The lack of dangling bonds at the MoS₂ surface may raise expectations for a weak Fermi level pinning (FLP) at the metal-MoS₂ interface and, thus, for a good control of the Schottky barrier height (SBH) with the metal work function (WF). However, the slope of the SBH versus WF curves has been experimentally reported to be as small as 0.09 [8]. Moreover, calculations based on Density Functional Theory (DFT) predict large densities of interface gap states (IGS) [9, 10], which are presumably responsible for the measured FLP.

In this paper, we report methodological guidelines and new DFT results for FLP and SBH in metal-MoS₂ contacts. We discuss the conditions for Fermi level de-pinning, which is a prerequisite for an engineering of the SBH and the attainment of an Ohmic behavior of the metal-MoS₂ contacts.

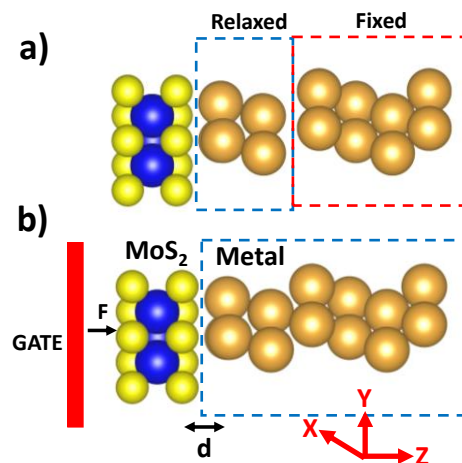


Fig. 1 : Simulation methods: (a) as in [9, 10], four metal layers are fixed and the two metal layers adjacent to MoS₂ are relaxed. (b) This work: fully relaxed stack. Here d is the metal-MoS₂ distance. A back gate is included to bias the system.

2. Simulation methodology and its validation

Quantum ESPRESSO is used to study the MoS₂ contacts with DFT [11]. The 111-surface of a six-layer metal crystal (Al or Au) is matched to a $\sqrt{3} \times \sqrt{3}$ MoS₂ monolayer supercell (x - y plane, Fig. 1) so as to minimize strain [10], and then relaxation is used to reduce residual forces on atoms [12]. The supercell includes a 1.5 nm thick vacuum region along z (Fig. 1) and we used dipole correction to minimize the spurious coupling with periodic replicas of the supercell [11]. We employed Projector augmented-wave (PAW) pseudopotentials to describe electron-ion interactions and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange and correlation functionals. Semi-empirical van der Waals corrections are included using DFT-D3 method. A back-gate is used to apply an electric field to the heterostructure along the z direction (Fig. 1b) [13, 14, 15].

Simulations fixing the position of the four top metal layers are reported in literature [9, 10], where only the two metal layers close to MoS₂ are relaxed (Fig. 1a). However, this may lead to artifacts in the dipole analysis. In fact, the dipole correction procedure uses an energy step (ΔV) to zero the field in vacuum [11]. Such ΔV value is often considered a measure of the charging of MoS₂ and it is also used to calculate the SBH [10]. But in the setup of Fig. 1a), the Au slab alone (MoS₂ is removed) has a sizeable ΔV in vacuum (black line, Fig. 2a), because of the mixture between fixed and relaxed atomic positions. The spurious ΔV of Au alone affects the ΔV and the SBH of the entire MoS₂-Au stack (red line), which has sometimes led to an overlooked artifact [9, 10].

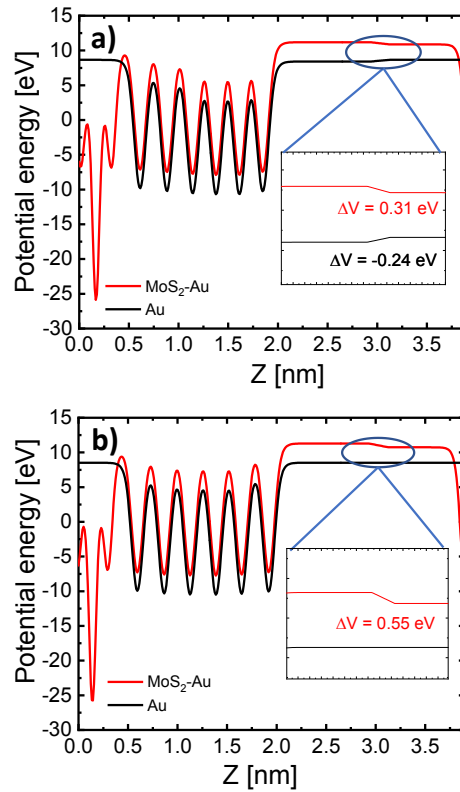


Fig. 2: Potential energy profiles of either Au alone or the MoS₂-Au stack. Steps in vacuum are used to zero the electric field due to dipoles in the stack. (a) Simulations as in Fig. 1a), where the non-homogeneous Au alone displays dipole effects (black line), affecting also the MoS₂-Au result (red line). (b) Results from the simulations as in Fig. 1b). Au alone does not display any dipole effect.

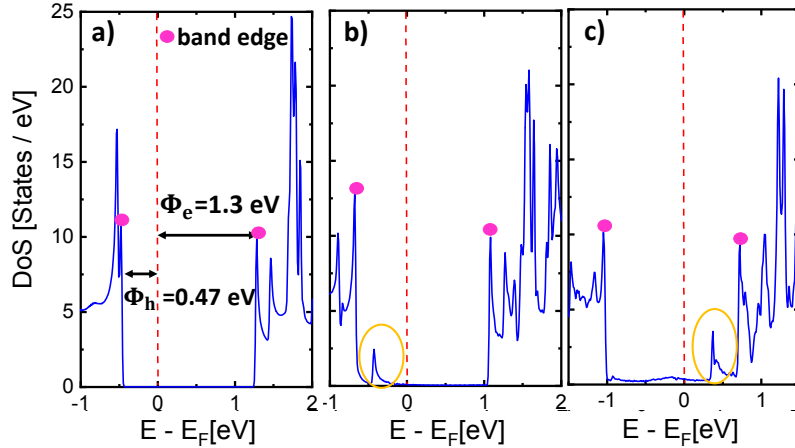


Fig. 3: PDoS of MoS₂ in the MoS₂-Au stack for (a) $d=0.8$ nm, (b) $d=0.4$ nm and (c) $d=0.3$ nm (MD). At short distances and, in particular at the MD, we see the onset of IGS (e.g. the large peaks marked by the yellow oval) that pin the Fermi level E_F inside the bandgap.

A more dependable procedure consists in relaxing the position of all atoms (Fig. 1b), and it has been used throughout this work. The Au slab alone now shows $\Delta V=0$ in vacuum (black, Fig. 2b). Thus the ΔV value of the entire MoS₂-Au stack (red) is a genuine signature of the dipole in the contact. Minimum energy distances (MD) between MoS₂ and Au (0.3 nm) or Al (0.27 nm) are obtained upon stack relaxation [10]. The calculated band structures of separated MoS₂, Au and Al have been also verified against literature data (not shown).

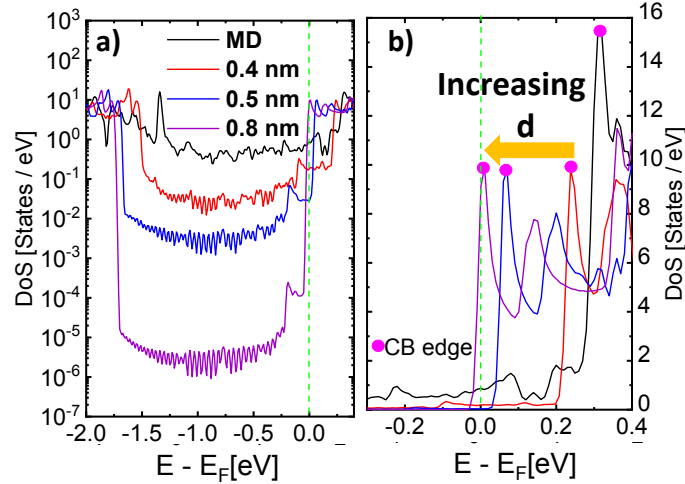


Fig. 4: PDoS of MoS₂ in MoS₂-Al stack for different d values in logarithmic (a) and linear scales (b, zoomed around E_F). For MD, E_F is pinned in the MoS₂ bandgap due to IGS (black). By increasing d , the IGS density is suppressed, so that E_F gets depinned and reaches the MoS₂ CB for $d=0.8$ nm.

3. Fermi level pinning and interface states

To evaluate the SBH and FLP, the partial density of states (PDoS) of MoS₂ is extracted for different distances, d , between MoS₂ and Au (Fig. 1). For $d=0.8$ nm (Fig. 3a), the PDoS of the MoS₂ layer is consistent with the isolated material ($E_{\text{gap}} \approx 1.8$ eV), with no IGS. Moreover, by defining the SBH for electrons/holes (Φ_e / Φ_h) as the difference between the conduction/valence band (CB/VB) edge and the Fermi level (E_F), the extracted SBH agrees well with the Schottky–Mott rule with a work function $\text{WF}=5.5$ eV for Au and a MoS₂ affinity of 4.2 eV. For shorter d values (Fig. 3b and c), instead, the IGS density increases considerably, thus pinning E_F and affecting the SBH. Similar results are observed for the MoS₂-Al stack (Fig. 4), with a large PDoS increase in the MoS₂ gap at small d (a), that pins E_F . For $d=0.8$ nm, instead, the SBH is about zero, consistently with $\text{WF}=4$ eV for the Al slab.

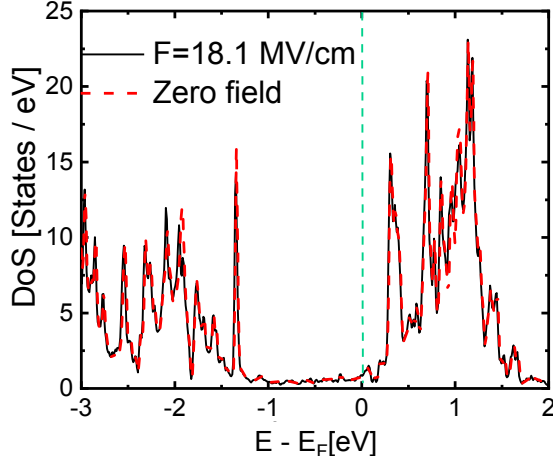


Fig. 5: PDoS of MoS₂ in the back gated MoS₂-Al stack at MD for $F=0$ and 18.1 MV/cm. E_F is strongly pinned and the electric field imposed by the back gate cannot influence E_F .

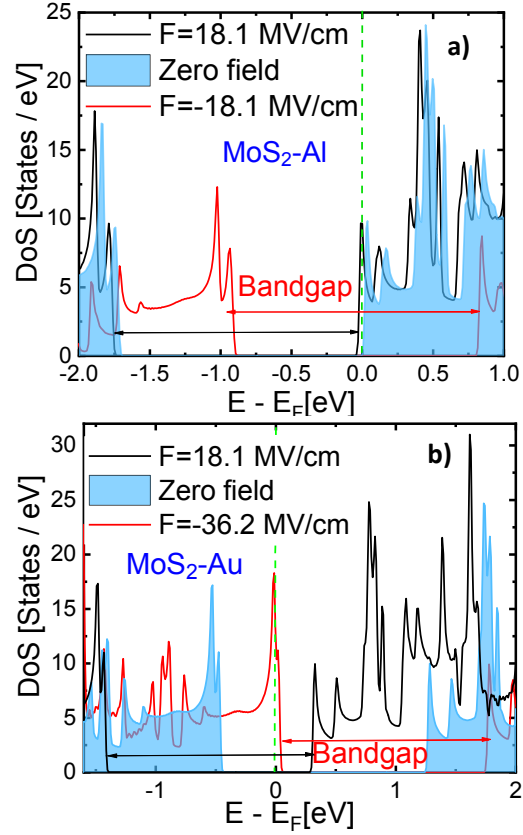


Fig. 6: **(a)** PDoS of MoS₂ in back gated MoS₂-Al at $d=0.8$ nm. E_F is de-pinned: the field shifts E_F with respect to CB and VB of MoS₂ (n-type contact for $F>0$). **(b)** PDoS in MoS₂-Au at $d=0.8$ nm. The field shifts E_F inside the MoS₂ bandgap (p-type contact for $F=-36.2$ MV/cm).

4. Back gated MoS₂ contacts

The back-gate in Fig. 1b) allows the biasing of MoS₂ through an external electric field (F). However, the strong FLP for small d values precludes any SBH modulation (Fig. 5). For $d=0.8$ nm, instead, due to the E_F depinning, the field can shift E_F with respect to the CB edge (Fig. 6), hence Φ_e reduces for $F>0$ and increases for $F<0$. To gain a better physical insight, we extracted the F induced charge in MoS₂ by using either the Bader analysis [13, 16] or simply the Gauss law; in fact, for $d=0.8$ nm, a dependable F value can be determined at both sides of MoS₂ from the potential energy profile (Fig. 7).

The charges extracted from Bader analysis or Gauss law agree well for MoS₂-Al (Fig. 8a) and MoS₂-Au (b). An electric field $F > 0$ increases the electron density in MoS₂ and eases the contact to the CB in the MoS₂-Al system, while a negative field eases a contact to the VB in the MoS₂-Au stack. It is worth mentioning that the apparently large F values needed to induce n-type or p-type contacts are due to the use of vacuum as a spacer between MoS₂ and the back-gate. By exploiting the dielectrics typically available in CMOS technologies, the required field can be reduced by a factor equal to the corresponding permittivity, namely of about 4 for SiO₂ and 30 for HfO₂.

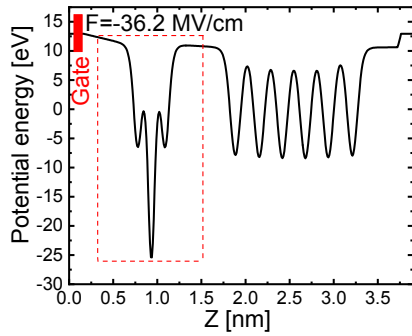


Fig. 7: Back gated MoS₂-Au stack. $d=0.8$ nm is large enough to calculate the field at both sides of MoS₂ (red dashed box).

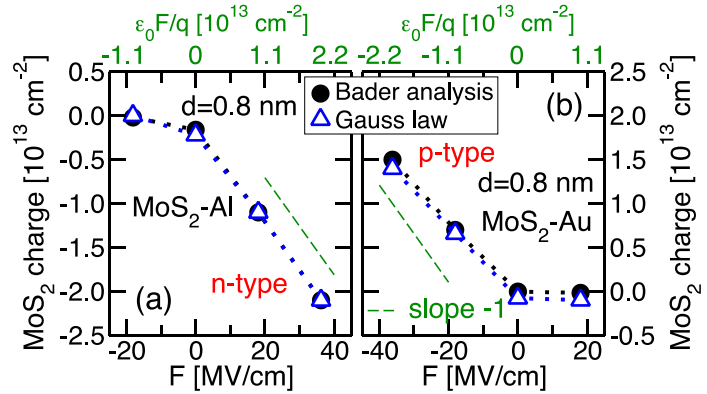


Fig. 8: MoS₂ charge vs. F extracted with Bader analysis or through the Gauss law for MoS₂-Al (a) and MoS₂-Au (b) stacks. The back gate field induces either an n-type (a) or a p-type contact (b).

5. Conclusions

The reported DFT results for FLP and SBH provide useful insights for the attainment of an Ohmic metal-MoS₂ contacts. The control of the distance d is crucial in order to enable a modulation of the SBH, that can be further adjusted by an effective back-gating of the structure. This may be achieved thanks to the insertion of a proper buffer layer such as graphene or h-BN between the metal and MoS₂. Such a possible engineering of the metal-MoS₂ contacts has been in fact explored in the recent literature, with some preliminary but encouraging results [17, 18].

Acknowledgments

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