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Schottky barrier heights and band alignments in transition metal dichalcogenides

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ABSTRACT

The Schottky barrier heights (SBHs) of metals on the layered transition metal dichalcogenides (TMDs) like MoS_2 are calculated by density functional theory using supercell models. Despite the presence of van der Waals bonding between the layers, the metals are found to bond quite strongly to the chalcogen sites in the top contact configuration, without disturbing the intralayer covalent bonding. This allows the SBHs to follow the metal induced gap state (MIGS) model that applies to regular 3D semiconductors, and gives a pinning factor $S \sim 0.3$. Additional pinning is caused by chalcogenide site vacancies. MoS_2 is found to favor n-type devices, because the pinning levels are in its upper gap. Other compounds like $MoSe_2$, WS_2 or WSe_2 have pinning levels around midgap, allowing ambipolar behavior.

1. Introduction

The transitional metal dichalcogenides (TMDs) layer compounds such as MoS_2 are important two-dimensional layered materials like graphene [1,2], but they have a band gap unlike graphene, and so can be useful as FETs. They are particularly relevant to end-of-roadmap logic devices like tunnel FETs (tFETs) [3]. Their intrinsic carrier mobilities are reasonably high but the performance of their devices seems to be limited by contact resistances [4–13]. It appears that most contacts possess a Schottky barrier instead of being ohmic. This leads to a desire to be able to control the Schottky barrier heights (SBHs) at the contacts by varying the contact metal, as is usual for semiconductors. It might be expected that this would be easy, because TMDs have van der Waals interlayer bonding, so there might also be weak bonding at the contact, which would lead to weak Fermi level pinning. In practice, this is not the case, and the Fermi level seems to be quite strongly pinned, according to the experimental data of Das et al. [7]. A second problem for MoS_2 is that E_F seems to be pinned in the upper part of the band gap [7], which strongly favors n-type devices. There is a desire for ambipolar devices, but it is unclear if these could be made from MoS_2, or if are different TMDs necessary for p-type devices [11]. Overall, it is clear that an improved understanding of the SBHs of TMDs is needed.

The overall behavior of SBHs is defined by variation of the n-type barrier height ϕ_n of the metal work function Φ_M which follows [14].

$$\phi_n = E_{cnl} - \chi + S(\Phi_M - E_{cnl}) \quad (1)$$

The important parameters are S and E_{cnl}. Here χ is the electron affinity of the semiconductor, Φ_M is the work function of the metal contract, E_{cnl} is the semiconductor's charge neutrality (CNL) reference energy, referred to the vacuum level, the energy up to which the MIGS are occupied on a neutral surface. S is the pinning factor $S = d\phi_n/d\Phi_M$, and it varies between $S = 1$ for unpinned interfaces (Schottky limit) to $S = 0$ for strongly pinned interfaces (Bardeen limit). Formally, S can be evaluated as [15].

$$S = \frac{1}{1 + \frac{N\delta e^2}{\varepsilon\varepsilon_0}} \quad (2)$$

where N is the areal density of gap states per eV, and δ is the decay length of the gap states into the semiconductor. For normal 3D semiconductors with a band gap of ~1.5 eV, S values are ~0.15, or strong pinning [15,16]. On the other hand, if at a top contact the contact was weakly bonded to the TMD, then N has decayed to a smaller value and S would increase towards 1.

2. Method

To check the actual behavior of TMD contacts, we studied them directly by density functional theory (DFT) calculations on

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supercells containing layers of metal and a monolayer of TMD or a block of TMD layers representing the bulk TMD [17]. We choose 6 layers of metal in the face centered cubic or body centered cubic structure. The (1 1 1) face of the metal is placed on a 2×2 hexagonal supercell of the TMD, and lattice matching is enforced. A symmetric supercell with no vacuum is used. The metal is allowed to relax along the vertical axis. The electronic structure is then calculated by the CASTEP plane wave DFT code, with the electronic interaction modeled by the generalized gradient approximation. A plane wave cutoff of 680 eV is used. The Grimme correction is applied to correct the error of DFT in describing van der Waals bonding. The band structures of the monolayer or bulk TMDs are also calculated in the screened exchange (sX) formalism [18], to correct the band gap error of DFT. It should be noted that the band gap of the monolayer TMDs is larger than the optical gap, because of a large exciton binding energy [19], due to the low screening. However, the presence of electrodes would add screening to the system. The CNL is calculated from the density of states, from the sX band structures.

3. Results and discussion

Fig. 1 plots the range of bond lengths observed at top contacts of various metals on an MoS_2 layer, vs the metal work function [20], and shows the bonding for a few cases. For reference, the Mo–S bond length is 2.41 Å. We see that contact metals such as Ti, Cr, Ni and Pd make quite short bonds to the outer S sites of the MoS_2 layer, but without disturbing the strong intra-layer bonding of the MoS_2 itself. Some metals such as Au, Ag, Al and In make weaker bonds. But overall, many top contacts form quite strong bonds to MoS_2, and not van der Waals bonds, as noted by others [21–23].

Fig. 2 plots the p-type Schottky barrier heights of metal top contacts on monolayer and bulk MoS_2, vs the metal work functions. The p-type Schottky barrier height is the energy from the TMD valence band maximum (VBM) to the metal Fermi level. In practice, this can be difficult to derive from the calculations, because of strong hybridization between the metal and chalcogenide states. Thus, we use the Mo 4 s semi-core level as a reference level and derive the energy of the metal E_f and the MoS_2 VBM with respect to this and thus the SBH as the difference.

In Fig 2, the pinning factor S is the slope of this line. We see that S has a similar value for both the monolayer (0.28) and the bulk material (0.33). This is found to be generally true. On the other hand, there is a sizeable displacement of the reference level E_{cnl} which is not just due to the change in band gaps. It is notable in Fig. 2 than we use metals with an extremely large range of work functions, from Sc at 3.5 eV to the degenerate semiconductor MoO_3 at 6.6 eV. The linearity of the fit is remarkably good.

The value of $S = 0.28$ for a monolayer compares to calculated values of ~0.3 found by Kang et al. [22], close to ours, but $S = 0.7$ eV found by Gong et al. [24]. The difference may arise from the different way of extracting the barrier heights in each work. Our value of $S = 0.3$ indicates moderate Fermi level pinning. However, it compares to a value of $S = 0.1$ found experimentally

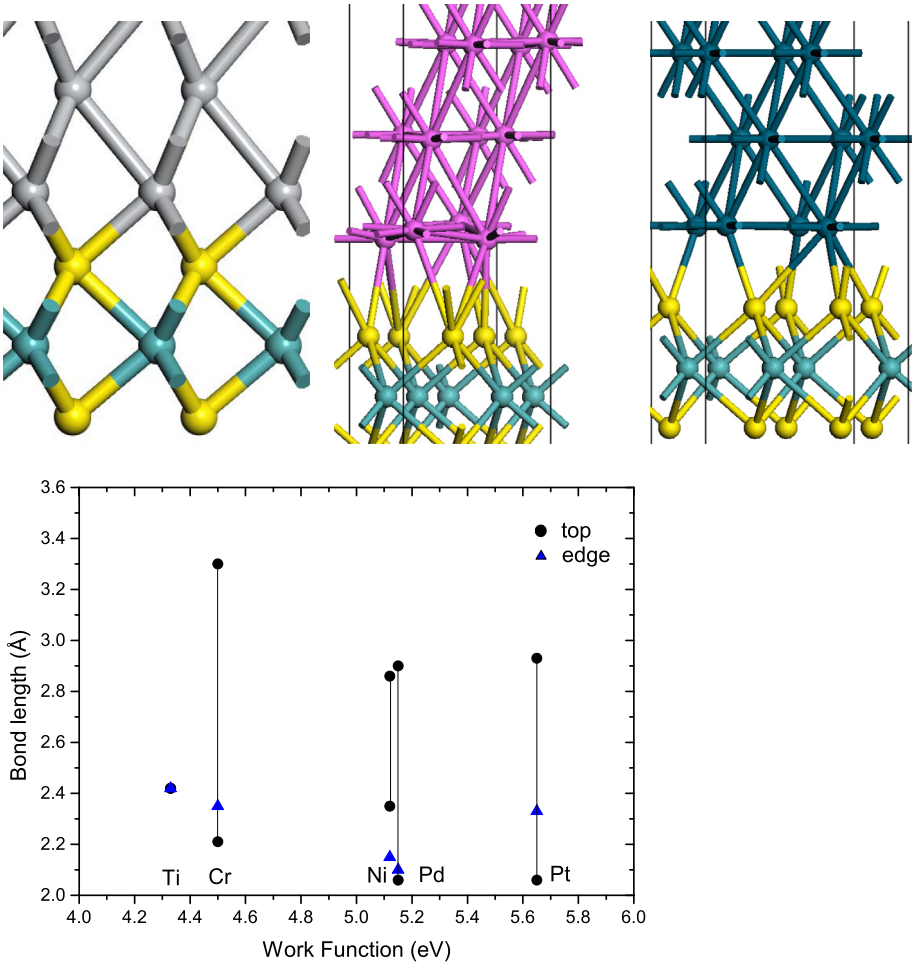

Fig. 1. (a–c) Structure of Ti, Cr and Ni contacts on MoS_2, (d) bond lengths of top contacts on MoS_2, showing short covalent bonds between electrodes and the TMD.

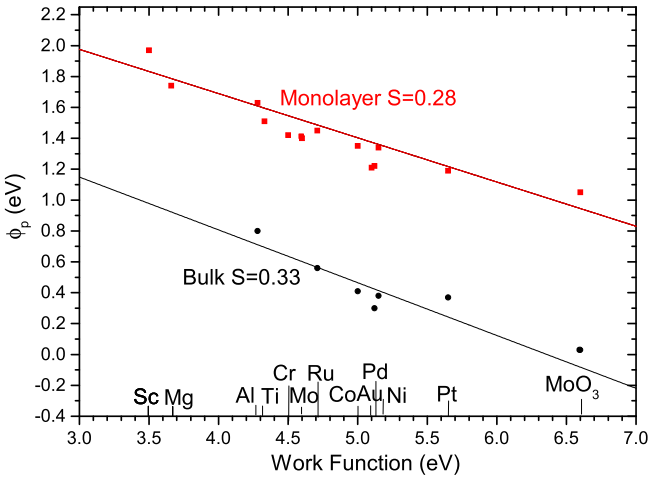

Fig. 2. Variation of p-type barrier height of monolayer and bulk MoS_2 vs metal work function.

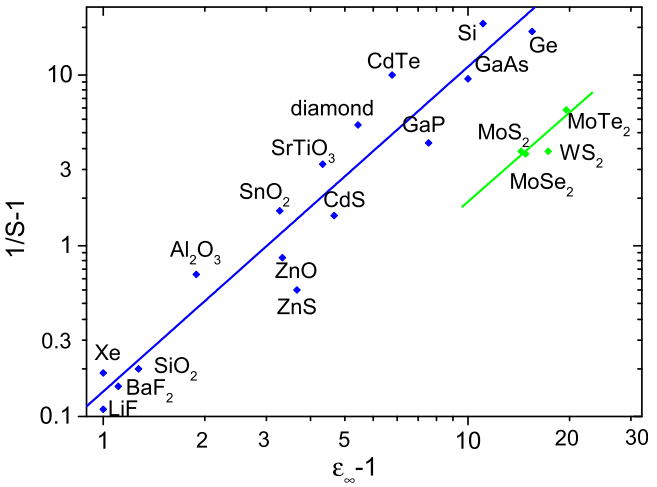

Fig. 4. Variation of Schottky barrier pinning factor *S* vs optical dielectric constant, showing consistency with the MIGS model.

by Das et al. [7], or strong pinning. The strong pinning must occur due to the presence of extra gap states, which would be due to defects.

Fig. 3 plots the calculated SBHs of different monolayer TMDs vs metal work function. The slopes are relatively similar, near 0.3, except for $MoTe_2$ which is lower.

As there is relatively strong bonding between contact and TMD layer (Fig 1), we have tested the standard model of Schottky barriers, the metal induced gap state (MIGS) model. This says that the main origin of the gap states doing the pinning are the evanescent states of the metal plane waves as they decay into the semiconductor band gap. In this model the *S* factor follows an empirical formula [14].

$$S = \frac{1}{1 + 0.1(\varepsilon_\infty - 1)^2} \tag{3}$$

where ε_∞ is the optical dielectric constant. Fig 4 plots our calculated *S* values vs the dielectric constant, using literature data. It is seen that they follow a straight line dependence, slightly shifted from the line for 3D semiconductors. This indicates that defect-free TMDs do follow the MIGS model.

We now consider the effect of defects. Defects give rise to gap states and if these are numerous, they can cause an additional pinning effect to MIGS states, which can reduce *S* and even shift the mean pinning energy away from the CNL energy. In MoS_2, S is bonded to three Mo's while Mo is bonded to six S's. Thus the formation energy of a Mo vacancy is much greater than that of a *S* vacancy, so *S* vacancies are the dominant defects [25,26]. Fig. 5 plots the energy levels of the chalcogen vacancies in each of the monolayer TMDs, with their bands aligned according to their CNLs. The CNLs tend to lie near midgap. For many of the TMDs, the chalcogen vacancy levels lie near midgap. It is seen that MoS_2 is anomalous in that its *S* vacancy level lies well into the upper gap, whereas for the other cases, the vacancy levels lie lower and nearer midgap. Thus, for bipolar operation, this figure suggests to use any other TMD except MoS_2.

The second point is that the vacancy formation energies have been calculated. A large formation energy will reduce the concentration of vacancies that form in any reaction with the electrodes. It is found that $MoTe_2$, WS_2 and WTe_2 have the highest vacancy formation energies. Thus these compounds will have fewer vacancies, and so their pinning factor will tend to be nearer that of MIGS alone, or $S = 0.3$, and not lowered to 0.1 as occurs for the case of MoS_2. The large effect of vacancies on the pinning in MoS_2 accounts for the strong deposition dependence found by McDonnell [13] and also accounts for the strong processing dependence of contact behavior found by many authors [27].

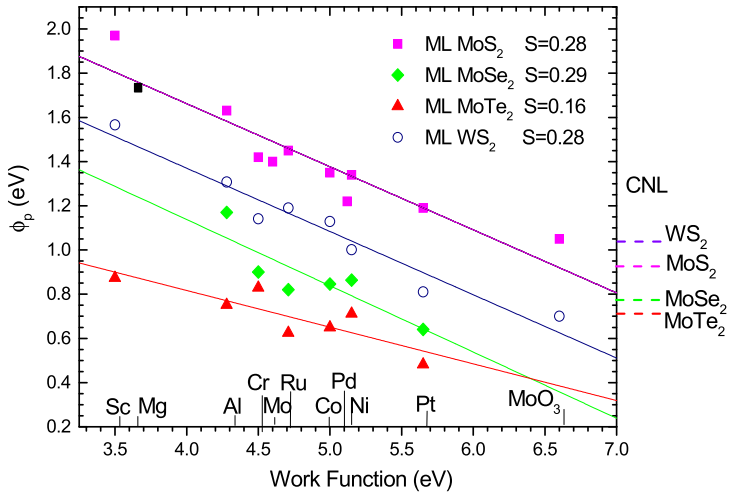

Fig. 3. Comparison of calculated p-type barrier heights for various metal dichalcogenides.

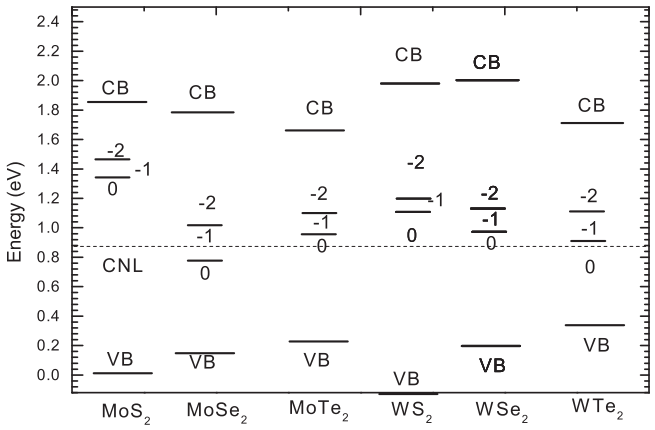

Fig. 5. Calculated charge neutrality levels (CNL) and anion vacancy transition levels for various TMDs, with bands aligned by their CNLs.

Finally, the band diagram of Fig 5 gives the band offsets between the various TMDs and can be used to give the band offsets as needed for tunnel FET applications.

The strong pinning means that it is difficult to change SBHs for MoS_2 simply by changing metal work function, or make p-type contacts on MoS_2 except by using exceptional high work function contacts like MoO_3. P-type devices should use the other TMDs whose CNLs lie nearer midgap.

In summary, we have calculated the Schottky barrier heights of various metals as top contacts on some TMDs. It is found that many metals make quite strong bonds to the TMD layers, and not van der Waals bonds. This gives rise to quite strong Fermi level pinning at their contacts, and the barrier heights follow the MIGS model. Additionally, reactions of the contacts with the TMD layers may create chalcogen vacancies which additionally pin E_F are reduce *S*.

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