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Schottky Barrier Heights and Band Alignments in Transition Metal Dichalcogenides

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Abstract

The Schottky barrier heights of transition metal dichalcogenides are calculated for ideal interfaces and found to be quite strongly pinned because the bonding of metals to MX2 layers is strong, not van der Waals. Sulfur vacancies cause additional pinning.

1 Introduction

Transitional metal dichalcogenides (TMD) like MoS_2 are important 2D materials [1]. Having a band gap unlike graphene, they can be used as FETs or end-of-roadmap devices like tunnel FETs [2]. However, their device performances are limited by contact resistances [3-8] due to Schottky barriers. Thus, we must understand Schottky barrier heights (SBHs) in TMDs. One might expect that their SBHs were weakly pinned due to van der Waals bonding. In practice, the Fermi levels are quite strongly pinned [4]. Also, E_F in MoS_2 is pinned in its upper band gap [4], favoring n-FETs. Thus, it is unclear if MoS_2 is unsuitable for ambipolar FETs, or different TMDs are needed [6].

The overall SBH behavior is defined by the variation of n-type barrier height ϕ_n with metal work function Φ_M [9].

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

Here χ is the semiconductor's electron affinity, E_{cnl} is its charge neutrality (CNL), referred to the vacuum level, the energy up to which the MIGS are occupied on a neutral surface. $S = d\phi_n/d\Phi_M$ is the pinning factor, and varies between S=1 for unpinned interfaces (Schottky limit) to S=0 for strongly pinned (Bardeen) limit. Formally, S is [10]

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

where N is the areal density of gap states per eV, and δ is their decay length into the semiconductor. For normal 3D semiconductors, S~0.15, or strong pinning [10]. 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 calculated the SBHs by density functional theory (DFT) using supercells containing layers of metal and a TMD monolayer (ML) or a block of layers representing bulk TMD.

3 Results and Discussion

Fig. 1 plots the range of bond lengths observed at top contacts of various metals on MoS_2 layers, vs the metal work function [11], 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 [12-14].

Fig. 2 plots the p-type Schottky barrier heights of top contacts on ML 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 E_F. In practice, this can be difficult to derive, because of strong hybridization between metal and TMD states. Thus, we use the Mo 4s semi-core level as a reference level to derive the metal E_f and MoS_2 VBM energies with respect to this.

In Fig 2, the pinning factor S is the slope of this line. We see that S has a similar value for both monolayer (0.28) and bulk material (0.33). This is true generally. It is notable in Fig. 2 than we use metals with a very wide range of work functions, from Sc (3.5 eV) to the degenerate semiconductor MoO_3 (6.6 eV). The fit linearity is remarkably good.

The value of S=0.28 for a monolayer compares to calculated values of ~0.3 by Kang [13] and ~0.3 by Gong [15]. Our value of S=0.3 indicates moderate Fermi level pinning. However, it compares to S=0.1 found experimentally by Das [4], or strong pinning. The strong pinning must be due to extra gap states, from 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 top contact and TMD layer (Fig 1), we 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 gap. In this model, S follows an empirical formula [9]

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

where ε_∞ is the optical dielectric constant. Fig 4 plots our calculated S values vs the dielectric constant, using literature data. 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 numerous, they 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 vacancies are the dominant defects [16]. 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 bi-polar operation, one should use other TMDs 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 [8] and also accounts for the strong processing dependence of contact behavior [8].

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

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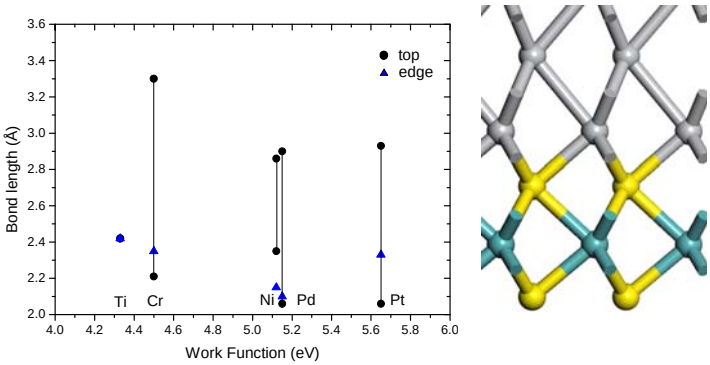

Fig. 1. Bond length between metal and S atoms of MoS2 top and edge-on contacts. Bonding at Ti-MoiS2 contacts.

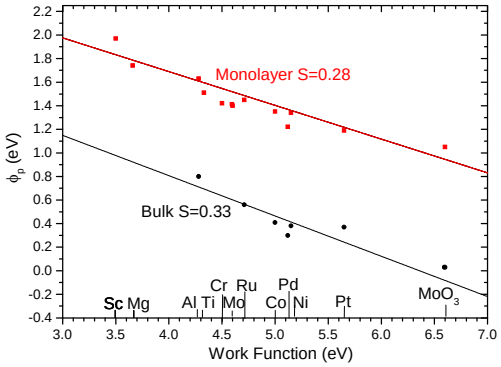

Fig.2. Schottky barrier heights vs. metal work functions, for top contacts on MoS_2.

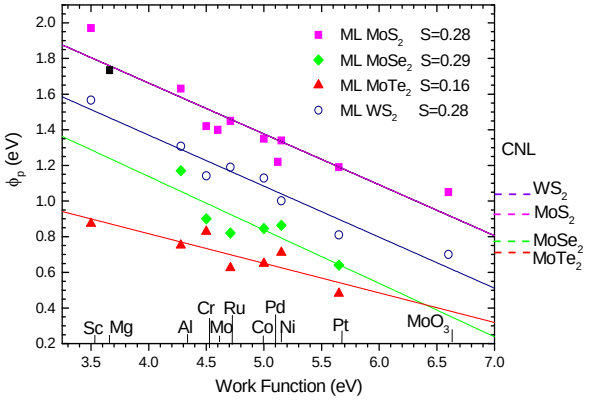

Fig. 3. SBHs vs metal work functions for top contacts on various TMDs.

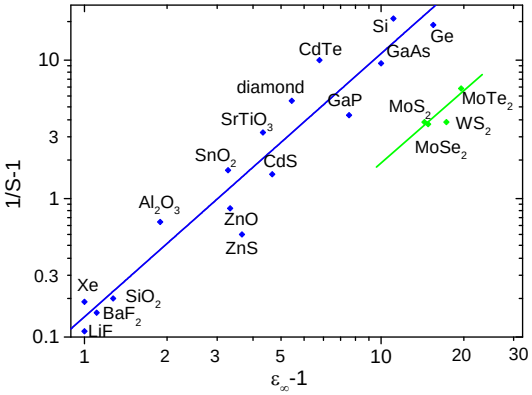

Fig. 4. Pinning factor S vs optical dielectric constant for 3D semiconductors and TMDs, both obeying MIGS model.

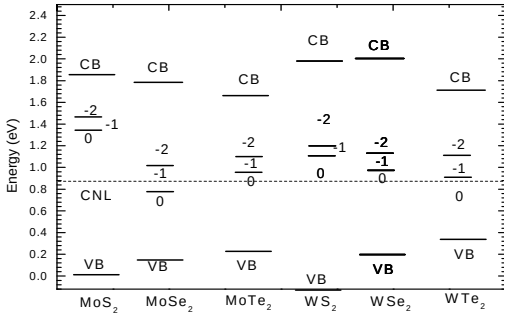

Fig 5. Carge neutrality levels (CNL) and anion vacancy transition levels for various TMDs, with bands aligned by their CNLs.