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Schottky Barrier Heights at Two-Dimensional Metallic and Semiconducting
Transition-Metal Dichalcogenide Interfaces

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Electrical Engineering

by

Adiba Zahin

December 2017

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Several advances have been made in the realization of electronic devices that utilize atomically thin two-dimensional (2D) materials. The semiconducting transition metal dichalcogenides in particular have been used to demonstrate a wide range of devices which include steep tunnel-field-effect transistors [1–6], photodetectors [7–12], field-effect-transistors [13–26] and chemical sensors [25, 27]. A variety of experimental [23, 28–37] and theoretical [38–43] studies have been devoted to understand the interface formed between the bulk metals that are deposited on the surface of the 2D transition metal dichalcogenides. There is growing evidence that the Schottky-like transport behavior observed in TMDC-metal contacts is a consequence of strong Fermi level pinning (FLP). The origin of the Fermi level pinning in metal-TMDC interfaces has been attributed to the formation of interface dipoles [41, 44], defects at the metal-TMDC interface and the existence of metal-induced-gap-states (MIGS) which arise from the exponential decay of the wavefunction of the metal Fermi level into the TMDC band gap [45,46]. One approach to minimize the effect of Fermi level pinning would be achieving an epitaxially clean interface between the metal and the semiconducting TMDC. Prior experimental studies of the contact resistance between the 2H/1T polytypes of
MoS$_2$ succeeded in demonstrating record low contact resistance [47]. A recent study shows that FLP is weak for the metal-semiconductor junction (MSJ) formed by van der Waals (vdW) interactions, which is attributed to the suppression of MIGS in the semiconductor [48]. All 2D contacts may allow the tuning of the Schottky Barrier (SB) height ($\phi$) by using different 2D metals.

To address this we investigate the use of 2D metallic TMDs (MX$_2$; M=Ta, Nb; X= S, Se,Te) as metal contacts instead of noble metals (Au, Pd, Ti, In etc) to 2D semiconducting TMDs (MX$_2$; M=Mo, W; X= S, Se,Te). We carry out a systematic study of the barrier heights and energy band lineups of the 2D semiconducting TMDs such as MoSe$_2$, WSe$_2$ and MoTe$_2$ with the 2D metallic TMDs such as NbS$_2$, NbSe$_2$, TaS$_2$ and TaSe$_2$ using ab initio density-functional theory (DFT) calculations. Using the calculated energy level alignments, we provide the values for the Schottky barrier heights for electron and hole injection for each combination of interfaces in vertical and lateral heterostructures.
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Chapter 1

Introduction and Goals

1.1 Introduction

As the silicon microelectronics industry is rapidly approaching to the point where devices can no longer be scaled to progressively smaller size, an alternative material to silicon is needed for future logic transistor applications. The International Technology Roadmap for Semiconductors (ITRS) predicts that additional new materials and transistor geometries will be needed to successfully address the formidable challenges of transistor scaling in the next 15 years [50–52]. Correspondingly, to sustain the compelling demand of lower power consumption with higher performance in electronic systems the quest for new materials is crucial. Graphene has attracted significant attention in the electronic materials community, but it lacks a band gap which makes it unsuitable for digital electronic applications [53, 54]. Consequently several classes of two-dimensional (2D) compounds including boron nitride, metal chalcogenides, oxides, hydroxides, and oxychlorides have also received recent attention. A comprehensive list of all known layered van der Waals solids has been reported in a number of recent reviews [28, 55–59]. However, only a few of these layered materials can be classified as
semiconductors and even fewer have been successfully isolated as airstable, high-quality, two-dimensional crystals.

Transition metal dichalcogenides (TMDCs) are among the most studied layered compounds as atomically thin films of semiconducting TMDs have recently been isolated and characterized. The TMDC family exhibits a wide range of electrical properties depending on the polytypes and the number of transition metal d-electrons which include metallic [60–63], half-metallic [64], semiconducting [13, 61, 65, 66], superconducting [67] and charge density wave [63, 68–71] behavior. Monolayer 2D crystal semiconductors have extremely small thicknesses (few Å) and pristine interfaces without out-of-plane dangling bonds allows for FET application, this efficient electrostatics, reduces short channel effects and provides fewer traps on a semiconductor-dielectric interface.

1.1.1 Layered 2D Transition Metal Dichalcogenide

Transition metal dichalcogenides (TMDs) are composed of transition metal and chalcogen atoms. According to the International Union of Pure and Applied Chemistry (IUPAC) definition, transition metals are elements with a partially filled d sub-shell or which can give rise to cations with an incomplete d sub-shell specially from Group VIB through VIIB. Ti, Zr, Hf, Nb, Ta, Mo, W, Tc, and Re are all transition metal elements that occur in TMDs [28,72,73]. These materials have strong in-plane covalent or ionic bonding and weak out-of-plane van-der-Waal forces which enables exfoliation into two-dimensional layers of monolayer thickness with the help of advance exfoliation and synthetic techniques [74–77]. This weak interlayer coupling changes the properties of these materials as their thickness approaches the monolayer limit. Often, the bandgap changes from direct to indirect as it moves from monolayer to multi-layer. The layered materials form different kinds of stacking orders due to the weak interlayer forces. The
different stacking configurations such as 1T, 2H\textsubscript{a}, 2H\textsubscript{b}, 2H\textsubscript{c}, 3R, 4H\textsubscript{a}, 6R etc result in a wide variety of electronic properties.

Experimental as well as theoretical studies shows that 2D layered materials have superior electronic, optical, mechanical and thermal properties than that of their bulk form [56, 58]. The self-passivated surfaces of these materials also makes it feasible to integrate heterostructures using different two dimensional materials and overcome limitations of dangling bonds associated with the growth and integration of unpassivated surfaces [78, 79].

1.1.2 Schottky Barrier

A Schottky barrier is a potential energy barrier for electrons formed at a metal-semiconductor junction (MSJ). Schottky barriers have rectifying characteristics, suitable for use as a diode. One of the primary characteristics of a Schottky barrier is the Schottky barrier height, denoted by $\Phi$. The value of $\Phi$ depends on the metal and semiconductor surface state, dangling bonds, Fermi level pinning (FLP) etc. [80]. The energy barrier height has a significant impact on device performance for charge carrier transport across the MSJ [80, 81]. $\Phi$ is defined as the energy difference between the Fermi level (FL) and the semiconductor band edges in the junction

$$\Phi_e = E_{CBM} - E_F$$

$$\Phi_h = E_F - E_{VBM}$$

Here, $\Phi_e$ and $\Phi_h$ are the barrier heights for electrons and holes respectively, $E_F$ is the Fermi energy and $E_{VBM}$ and $E_{CBM}$ are the energy of the valence band maximum (VBM) and conduction band minimum (CBM) of the semiconductor in the junction. Neglecting the metal-semiconductor interaction, $\Phi$ should ideally follow the predictions
Figure 1.1: (a) Work function of metal; electron affinity and ionization potential of semiconductor. (b,d) are two possible n-type Schottky barriers ($\Phi_e$); (c,e) are two possible p-type Schottky barriers ($\Phi_h$).
of the Schottky-Mott model

\[ \Phi_e = E_{ea} - W \]  

\[ \Phi_h = W - E_{ip} \]  

(1.3)  

(1.4)

where, \( W \) is the work function of the metal, and \( E_{ea} \) and \( E_{ip} \) are the electron affinity and ionization potential of the semiconductor in the junction. The work function of the metal, the electron affinity and the ionization potential of semiconductor are shown in Fig. 1.1(a). Fig. 1.1 also demonstrates the two possible n-type (b,d) and p-type (c,e) Schottky barrier heights.

1.2 Motivation and Goals

1.2.1 Contact Resistance

Experience shows that the access to a semiconductor region via a metal contact usually exhibits higher resistance than expected from an ideal contact. The additional resistance may be viewed as being a series resistor in the lead to the ideal contact. It shall be referred to as "contact resistance" [82]. If actual contact resistance is \( R_a \) and the ideal contact resistance is \( R_i \) then the contact resistance is then defined by the difference of these two resistances [82].

\[ R_c = R_a - R_i \]  

(1.5)

Contact resistance in the context of a metal/semiconductor heterostructure is the resistance contributed by the interface formed between the metal and semiconductor. In the case of a Schottky contact, the contact resistance is primarily contributed by thermionic and field emission over and across the Schottky barrier height and gives rise to rectifying behavior in current versus voltage. In an Ohmic contact in principle there is no barrier,
so the current versus voltage characteristics are linear and determined by the quality of
the interface. This of course is an oversimplification and neglects several complications
that can arise in experiments, eg. interface traps, roughness, etc

Contact resistance is a crucial determinant of FET performance. Low contact
resistance in 2D semiconductor based devices is critical for achieving high on-state cur-
rent, large photoresponse [7] and high-frequency operation [83]. Electrical metal contacts
to two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDCs) are
found to be the key bottleneck to the realization of high device performance due to
strong Fermi level pinning and the contact resistances ($R_c$) [84].

1.2.2 Fermi Level Pinning

Fermi level pinning refers to a situation where the band bending in a semicon-
ductor contacting a metal is essentially independent of the metal even for large variation
in the work function of the metal. A variety of experimental [23, 29, 85] and theoretical
[41,42] studies have been devoted to understanding the interface formed between the
bulk metals that are deposited on the surface of the 2D transition metal dichalcogenides.
There is growing evidence that the Schottky-like transport behavior observed in TMDC-
metal contacts is a consequence of strong FLP. The origin of the FLP in metal-TMDC
interfaces has been attributed to the formation of interface dipoles [41,44], defects at
the metal-TMDC interface and the existence of metal-induced-gap-states (MIGS) which
arise from the exponential decay of the wavefunction of the metal Fermi level into the
TMDC band gap [45,46].

One approach to minimize the effect of Fermi level pinning would be achieving
an epitaxially clean interface between the metal and the semiconducting TMDC [86].
High performance WSe$_2$ field effect transistors were demonstrated using van der Waals
assembly of substitutionally doped [26] and mixed-composition atomic layers between semiconducting and metallic TMDCs [87]. Experimental results show that NbSe$_2$ results in nearly ohmic p-type contacts to WSe$_2$ [88, 89]. TaSe$_2$ has also been demonstrated to be a low-resistivity contact to semiconducting TMDCs (s-TMDCs) (MoSe$_2$ and HfSe$_2$) [90]. An experimental and theoretical study identified and proposed Mo$^{5+}$-rich interface region to have low hole Schottky barriers utilizing MoO$_x$ contacts on MoS$_2$ and WSe$_2$ [91]. They suggest controlling the purity and stoichiometry of MoO$_x$ will be key in realizing the potential of MoO$_x$ as an efficient Ohmic hole injection contact. Experimental study have shown high performance, large-scale devices and circuits based graphene/MoS$_2$ heterostructure. They claim the tunability of the graphene work function with electrostatic doping significantly improves the ohmic contact to MoS$_2$ [92]. A very recent theoretical study also shows that the planar boron sheets (S1 and S2) are good candidates to form p-type Schottky contacts with the TMDCs (MoSe$_2$ and WSe$_2$) which can be tuned to a p-type ohmic contact upon an external electric field [93]. Prior experimental study have demonstrated record low contact resistance between the 2H/1T polytypes of MoS$_2$ [47]. They have demonstrated that the metallic 1T phase of MoS$_2$ can be locally induced on semiconducting 2H phase nanosheets, thus decreasing contact resistances to 200-300 $\mu$m at zero gate bias. They shoes the phase engineering can markedly reduce the contact resistance between the source/drain electrodes and the channel to enable high-performance FETs. Experimental study have also demonstrated true ohmic contact between 2H/1T$'$ phase of MoTe$_2$ [94]. These suggest that pristine metal TMDC interfaces offer a route to more transparent contacts.
1.2.3 Metallic Transition Metal Dichalcogenide

The Group V TMDCs are metallic in nature for all thicknesses from monolayer to bulk, and they exhibit the same self-passivated atomic structure as the Group VI TMDCs. An interface formed between a metallic and semiconducting TMDC would in principle be free of interface defects and this would lead to a reduction in the strength of the Fermi level pinning at the interface. A recent study shows that FLP is weak for the metal-semiconductor junction (MSJ) formed by van der Waals (vdW) interactions, which is attributed to the suppression of MIGS in the semiconductor [48]. It might allow the tuning of the Schottky Barrier (SB) height (\(\phi\)) by using different 2D metals. They have predicted NbS\(_2\) to be the most promising electrode with s-TMDCs [48].

Among the 2H family of transition metal dichalcogenides, NbS\(_2\), NbSe\(_2\), TaS\(_2\), TaSe\(_2\) are metallic in their nature [60, 61, 95]. Experimental study shows that, TaS\(_2\) devices remained metallic despite the fabrication process [96]. Theoretical work shows that both monolayer NbX\(_2\) and TaX\(_2\) are metal. The NbS\(_2\) sheet exhibits metallic behavior with one band crossing the Fermi level. The partial DOS analysis indicates this band is mainly attributed to the d orbitals of Nb atoms. Since the Nb (Ta) atom is one d electron less than the Mo (W) atom, the top d-character valence bands are not fully occupied and the metallicity appears in the monolayer NbX\(_2\) (TaX\(_2\)) [97]. This result is consistent with the experimental observation that the TaS\(_2\) films present robust metallic behaviors [96]. Thus, these monolayer metallic NbX\(_2\) and TaX\(_2\) would be one type of conducting materials for nano-devices [97].

Using a 2D metal as an electrode has other benefits. A 2D metal has limited electronic density of states (DOS) which gives low quantum capacitance. Thus, when charge is accumulated by applying a dielectric-mediated voltage, its work function (\(W\))
changes markedly compared with conventional metals. This unique feature of a 2D metal leads to a gate-tunable $W$ and therefore Schottky barrier (SB) height $\Phi$, which have been observed in experiments [92, 98–101]. The interface between the metal and the semiconductor is flat, which could facilitate carrier transport [86]. This atomically flat interface is difficult to achieve by using conventional metals. The suppression of MIGS reduces the electron-hole recombination at the interface, leading to a higher energy conversion efficiency for optoelectronic devices.
Chapter 2

Theoretical Methods

Density functional theory (DFT) is a computational quantum mechanical modeling method used to investigate the electronic structure of many-body systems particularly atoms, molecules and the condensed phases. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics and computational chemistry. DFT allows the many-electron Schrödinger equation to be solved in practice. The foundation of density functional theory are the Hohenberg-Kohn (HK) theorems [102]. The first HK theorem proves that the ground-state of a many-electron system is uniquely determined by the electron density of the system. The second HK theory states the total ground-state energy of such a many-electron system is a functional of the ground-state electron density. The Kohn-Sham approach [103] made the HK theorems computationally tractable. Within the framework of Kohn-Sham DFT (KS DFT), the many-body problem of interacting electrons in a static external potential is reduced to a problem of non-interacting electrons moving in an effective potential [103]. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation in-
teractions. Basically, the Kohn-Sham approaches replaces the many-body electron wave function with a non-interacting system in an effective potential that has a ground state density that is identical to that of the many-body interacting system. Two common approaches to approximate the exchange correlation potential include the local density approximation (LDA) and the generalized gradient approximation (GGA) [104, 105]. The main rationale behind these approximations is that for electron densities within a solid, exchange and correlation effects occur on a short length scale. Hence, LDA and GGA approximations of DFT accurately describe the properties of materials that resemble a homogeneous electron gas.

First-principles calculations of the TMDC heterostructures were carried out using DFT with a projector augmented wave method and the Perdew-Burke-Ernzerhof (PBE) type GGA [104, 105] as implemented in the Vienna Ab Initio Simulation Package (VASP) [106]. A plane wave cutoff of 500 eV was used for all calculations. For each heterostructure the structural relaxation was performed until all forces were converged below 10 meV/Å. The workfunctions of the m-TMDs are determined using explicit slab calculations and the results are summarized in Fig. 3.1. For the slab calculations, a vacuum distance of 15 Å was used for each monolayer material. Then the difference between the electrostatic potential in the vacuum region and at the Fermi level gives us the workfunction \( V_{\text{vacuum}} - E_F \). Theoretical methods are covered in more detail in Chapter 3.3.1 and 3.4.1.
Chapter 3

Results and Discussions

3.1 Identifying the appropriate combination of the metal and semiconducting TMDC

Our investigations of the interface between the metal-semiconducting TMDCs first rely on identifying the appropriate combination of the metal and semiconducting TMDC which results in the lowest bi-axial, in-plane strain. Table 3.1 shows the lattice constant for the different materials investigated as part of this study and the calculated results are consistent with previous experimental and theoretical studies [97, 107–111]. The strain associated with the combination of the metallic and semiconducting TMDCs are shown in Table 3.1. We have relaxed each material to their ground state energy.
Table 3.1: In-plane lattice constants, $a_0$, of the metallic & semiconducting TMDCs and the lattice mismatch associated with combinations of each material. Lattice mismatch values that are less than 2% have been highlighted in bold.

<table>
<thead>
<tr>
<th></th>
<th>MoSe$_2$</th>
<th>MoTe$_2$</th>
<th>WSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$(Å)</td>
<td>3.31</td>
<td>3.53</td>
<td>3.34</td>
</tr>
<tr>
<td>Lattice mismatch (%)</td>
<td>1.21</td>
<td>5.10</td>
<td>0.30</td>
</tr>
</tbody>
</table>

and have compared their lattice constants to find the lattice mismatch among them. We identify the combinations of semiconducting and metallic TMDCs that have a lattice mismatch lower than 5%. The metallic-TMDCs (m-TMDCs) occur in octahedral (1T) and trigonal-prismatic (2H) polytypes while the s-TMDCs have a trigonal prismatic (2H) coordination in their ground state. In our study we consider heterostructures with the m-TMDCs that have trigonal-prismatic coordination.

### 3.2 Band alignment of MX$_2$ and Workfunction of metal

The work functions of the m-TMDCs are in general larger than the work function of the noble metals that are conventionally used as contacts with the s-TMDCS [23,49]. We have calculated the workfunction of each 2D metallic TMDC (MX$_2$; M=Nb, Ta; X= S, Se) and align them with respect to vacuum other noble metals [23,49] along with the calculated band alignment of 2D s-TMDCs (MoSe$_2$, MoTe$_2$, WSe$_2$), which is illustrated in Fig. 3.1. This large work function could be advantageous for good p-type contacts to the 2D semiconductors. Fig. 3.1, also shows the expected line-up of the m-TMDC Fermi levels with the bands of the s-TMDCs. All of the metallic TMDs are expected to have little to no barrier with the s-TMDC valence bands facilitating low-
Figure 3.1: Calculated band alignment of MX$_2$ and work function of the metallic TMDCs along with the work function of noble metal from [23,49]. The vacuum level is taken as zero reference.

We have calculated the band alignments of these metal-semiconducting heterostructures using explicit interface calculations. For each heterostructure, the valence and conduction band offset is obtained by calculating the electronic band structure and identifying the band extrema contributed by the semiconducting and metallic TMDC.

3.3 Vertical Heterostructure

Fig. 3.3 demonstrates the vertical heterostructure with monolayer m-TMDC and monolayer s-TMDC. Fig. 3.3(a,b) are the side view and Fig. 3.3(c,d) are the top view of 2H$_b$ and 2H$_c$ stacking respectively. Here we have consider the following heterostructures: MoSe$_2$-NbS$_2$, MoSe$_2$-NbSe$_2$, MoSe$_2$-TaS$_2$, MoTe$_2$-NbSe$_2$, MoTe$_2$-TaSe$_2$. 

resistance hole injection to the s-TMDCs. Graphically which can be represented by Fig. 3.2.

We have calculated the band alignments of these metal-semiconducting heterostructures using explicit interface calculations. For each heterostructure, the valence and conduction band offset is obtained by calculating the electronic band structure and identifying the band extrema contributed by the semiconducting and metallic TMDC.

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Figure 3.2: (a) Band diagram of metal and semiconductor with respect to vacuum, (b) possible band bending after contacting the metal and semiconductor.

WSe$_2$-NbS$_2$, WSe$_2$-NbSe$_2$ and WSe$_2$-TaS$_2$. We then calculate the band alignments of these metal-semiconducting heterostructures using explicit interface calculations.

### 3.3.1 Methodologies

In the vertical heterostructure to account the van-der-Waal interactions, the semiempirical Grimme-D2 [112] method was applied. We calculated the total energy verses lattice constant for each heterostructure and found the lowest energy structure to be the one in which the in-plane lattice constant of the heterostructure is the average of the two. Therefore, we used the average lattice constant of s-TMDCs and m-TMDCs. The lowest energy stacking polytype was used for each structure. The heterostructures are in the lowest energy for 2H$_b$ stacking (Fig. 3.3(a,c)) with the exception of MoTe$_2$-TaSe$_2$, which has lowest energy in 2H$_c$ stacking (Fig. 3.3(b,d)). A Monkhorst-Pack scheme [104] with $16 \times 16 \times 2$ k-point grid was used for the structural relaxation and $8 \times 8 \times 1$ k-point grid was used for self consistence field calculation.
Figure 3.3: Vertical heterostructure with monolayer m-TMDC and monolayer s-TMDC. (a,b) are the side view and (c,d) are the top view of 2H$_b$ and 2H$_c$ stacking respectively.

3.3.2 Results

Fig. 3.4 shows the electronic band structure of all the metal-semiconductor heterostructures. Each $k$-point of each band is color coded according to its maximum orbital weight on each atom. All the materials along with their orbitals are color coded in Fig. 3.4. We have taken the Fermi energy as reference. The metal bands cross the Fermi energy. The closest band from s-TMDCs which lies below the Fermi level is the valence band and the closest band from s-TMDCs which lies above the Fermi level is the conduction band. The valence band offsets (VBO) are identified by calculating the energy difference between the s-TMDC valence band (d-orbital of Mo/W) and the Fermi energy. The VBO are shown with pink arrows. Similarly the conduction band offset (CBO) is identified by calculating the energy difference between the s-TMDC conduction band (d-orbital of Mo/W) and the Fermi energy. The green arrows of Fig. 3.4 represent the CBO. The valence band of the s-TMDCs in the heterostructure combination are $0.131 - 0.475$ eV below the Fermi level. The conduction band of the s-TMDCs in the
heterostructure combination are $0.762 - 1.318$ eV above the Fermi level.

![Electronic bandstructure of the metal-semiconductor heterostructures](image)

Figure 3.4: Electronic bandstructure of the metal-semiconductor heterostructures; (a)MoSe$_2$-NbS$_2$, (b)MoSe$_2$-NbSe$_2$, (c)MoSe$_2$-TaS$_2$, (d)MoTe$_2$-NbSe$_2$, (e)MoTe$_2$-TaSe$_2$, (f)WSe$_2$-NbS$_2$, (g)WSe$_2$-NbSe$_2$ and (h)WSe$_2$-TaS$_2$.

The VBO is significantly lower than the CBO. This trend occurs independent of the chalcogen or transition metal ion that constitutes the semiconducting or metallic TMDC. This can be understood by considering the alignment of the valence bands of the s-TMDCs and the m-TMDCs on an absolute scale as shown in Fig. 3.1. The large work function of the m-TMDCs leads to their Fermi level always near to the s-TMDCs.
Fig. 3.5: Conduction and Valance Band Offsets in the interface of monolayer Metal-monolayer Semiconductor heterostructure.

valence band.

Fig. 3.6(a,b,d,e) demonstrates, the charge density difference, $\Delta \rho = \rho(\text{metallic/semiconducting TMDC}) - \rho(\text{m-TMDC}) - \rho(\text{s-TMDC})$ with their corresponding band structure. A surplus of electrons are shown in yellow near the m-TMDCs, and a deficiency of electrons are shown in blue near the s-TMDCs Fig. 3.6(a,d). The red color in Fig. 3.6(b,e) represents $\Delta \rho$ in the s-TMDC layer, and the blue color represents $\Delta \rho$ in the m-TMDC layer. The transfer of charge from the s-TMDC layer to the m-TMDC layer is consistent with the large work functions of the m-TMDCs shown in Fig. 3.1.

In conclusion, we have studied the band alignments between the semiconducting and metallic transition metal dichalcogenides from first principles. Our calculations highlight the ability to achieve interfaces with low valence band offsets between the semiconducting and metallic TMDCs. Such heterostructures could facilitate low resistance p-type contacts to monolayers semiconducting TMDCs.
Figure 3.6: Charge transfer, charge density difference $\Delta \rho$, and electronic band structure at the interface of (a-c) WSe$_2$-NbS$_2$; (d-f) MoSe$_2$-NbSe$_2$ heterostructure.

3.4 Lateral Heterostructure

Lateral heterostructures have also been demonstrated in TMDCs [113, 114]. Therefore, we also consider lateral 2D metal-semiconductor heterostructures for all 2D contacts. We have studied the effects of interfaces formed between transition metal dichalcogenides by in-plane covalent bonds, with similar and dissimilar chalcogen atoms. Fig. 3.7(a) shows the lateral heterostructure of a monolayer m-TMDC and a monolayer s-TMDC formed by in-plane covalent bonds. Two type of interface geometries are considered, armchair and zigzag, as illustrated in Fig. 3.7(c,d). To create the armchair and zigzag interface, we start with the rectangular unit cell shown in Fig. 3.7(b) instead of the hexagonal primitive unit cell. We repeat the rectangular unit cell along the
Figure 3.7: (a) Side view; top view of (c) an armchair interface and (d) a zigzag interface of lateral metal-semiconductor heterostructure. (b) Rectangular unit cell

It is shown in Fig. 3.7(c), and we repeat it along the $b$ axis to obtain the zigzag interface shown in Fig. 3.7(d). The dotted lines in Fig. 3.7(c,d) show the unit cell of each heterostructure configuration. The unit cell is periodic in all directions. We repeat the rectangular cell of Fig. 3.7(b) eight times to obtain four layers of metallic TMDCs and four layers of semiconducting TMDCs. The lattice vector $a$ of the rectangular unit cell is smaller than the lattice vector $b$, so the armchair heterostructure is smaller than the zigzag heterostructure.

Fig. 3.8 shows the rectangular Brillouin zone (BZ) in purple corresponding to the rectangular unit cell of Fig. 3.7(b) tiled over the hexagonal BZ of the hexagonal primitive unit cell in red. The $K$ and $K'$ points in the hexagonal BZ (H-BZ) are shown...
Figure 3.8: Hexagonal (red) and rectangular (purple) Brillouin zone (BZ). The \( K \) and \( K' \) points in the hexagonal BZ are shown in red. The \( X', X \) points in the rectangular BZ are shown in purple. The \( \Gamma \) and \( M \) points are the same in both hexagonal and rectangular BZ shown in green. The \( K \) and \( K' \) points maps back to rectangular BZ shown in blue.

in red. The \( X', X \) points in the rectangular BZ (R-BZ) are shown in purple. Four of the H-BZ \( M \) points map onto the corners of the R-BZ, and two of the H-BZ \( M \) points map back to \( \Gamma \) in the R-BZ. The \( K \) and \( K' \) points in the H-BZ lie in the extended zone of the R-BZ. This results in a mapping back of the the six \( K \) and \( K' \) points to the \( \Gamma-X' \) line in the R-BZ shown in blue. In Fig. 3.8, \( g_1 \) and \( g_2 \) are the reciprocal lattice constants of the H-BZ of MoSe\(_2\). The reciprocal lattice constants of the R-BZ are \( g'_1 = g_1 + \frac{1}{2}g_2 \)

and \( g'_2 = \frac{1}{2}g_2 \).

3.4.1 Methodologies

For each material system and each interface geometry, we considered two structures, one with the s-TMDC strained coherently to the m-TMDC and the other with m-TMDC strained coherently to the s-TMDC. For both, a complete internal relaxation
of all of the atomic coordinates was performed. A $1 \times 6 \times 1$ Monkhorst-Pack scheme [104] was used for the armchair heterostructure and a $6 \times 1 \times 1$ Monkhorst-Pack scheme was used for the zigzag heterostructure relaxation and self consistency field calculation. Two metal-semiconductor heterostructures are considered, MoSe$_2$-TaS$_2$ and WSe$_2$-NbSe$_2$.

### 3.4.2 Results

![Rectangular unit cell and electronic band structure](image)

**Figure 3.9:** (a) Rectangular unit cell and the electronic band structure of monolayer (b) MoSe$_2$, (c) TaS$_2$, (d) WSe$_2$ and (e) NbSe$_2$ rectangular unit cell.

Before investigating the heterostructures, we first plot the electronic bandstructure of the 4 different materials calculated using the rectangular unit cell of Fig. 3.9(a). Fig. 3.9(b-e) are the electronic band structures of the rectangular unit cells of MoSe$_2$, TaS$_2$, WSe$_2$ and NbSe$_2$, respectively. The VBO and the CBO of the two s-TMDCs are
Figure 3.10: Atomistic supercells simulated for in-plane, monolayer heterojunctions with an armchair interface and a zigzag interface. (a) The rectangular unit cell of armchair interface and (b) the corresponding BZ. (c) The rectangular unit cell of zigzag interface and (d) the corresponding BZ. The corresponding E-k relation is shown under each supercell with the bands color coded to show the atom with the maximum projected density of states as given in the legends. (e,f) MoSe$_2$ is strained to match the lattice constant of TaS$_2$. (g,h) TaS$_2$ is strained to match the lattice constant of MoSe$_2$. (i,j) WSe$_2$ is strained to match the lattice constant of NbSe$_2$. (k,l) NbSe$_2$ is strained to match the lattice constant of WSe$_2$. 

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Table 3.2: VBO and CBO in the lateral heterostructure.

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>MoSe$_2$-TaS$_2$</th>
<th>WSe$_2$-NbSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface</td>
<td>MoSe$_2$ is strained to match the lattice constant of TaS$_2$</td>
<td>TaS$_2$ is strained to match the lattice constant of MoSe$_2$</td>
</tr>
<tr>
<td>Armchair</td>
<td>k-path</td>
<td>$\Gamma - X'$</td>
</tr>
<tr>
<td></td>
<td>VBM</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>k-path</td>
<td>$X'$</td>
</tr>
<tr>
<td></td>
<td>CBM</td>
<td>1.479</td>
</tr>
<tr>
<td>Zigzag</td>
<td>k-path</td>
<td>$\Gamma - X'$</td>
</tr>
<tr>
<td></td>
<td>VBM</td>
<td>-0.066</td>
</tr>
<tr>
<td></td>
<td>k-path</td>
<td>$\Gamma - X'$</td>
</tr>
<tr>
<td></td>
<td>CBM</td>
<td>1.410</td>
</tr>
</tbody>
</table>

shown with green and red arrows, respectively, and they occur along the $\Gamma - X'$ line as discussed above.

The electronic band structure of the heterostructures are shown in Fig. 3.10. The heterostructure unit cells are shown in Fig. 3.10(a,c), and the corresponding electronic band structure for the two different material combinations and strain are shown below. The rectangular BZs corresponding to the heterostructure unit cells are shown in Fig. 3.10(b,d). From the electronic band structure in the Fig. 3.10(e-l), we extract the CBO and VBO formed at the interface of two lateral heterostructures each in two different strain conditions. Fig. 3.10(c,e) shows a band with primary contribution from the Mo atom of the MoSe$_2$-TaS$_2$ heterostructure lying at the Fermi level. This indicates that the valence band of MoSe$_2$ lies at the Fermi level of TaS$_2$ in this horizontal armchair heterojunction configuration providing a zero-barrier contact for holes. Similarly, the valence band of WSe$_2$ lies at the Fermi level of NbSe$_2$ in the armchair WSe$_2$-NbSe$_2$ heterostructure as shown Fig. 3.10(i,k). Table 3.2 shows all of the magnitudes and positions of the VBO and CBO of the lateral heterostructure.
Figure 3.11: Valence band offsets of the lateral metal-semiconductor heterostructures.

The valence band offsets from the heterostructure calculations are shown in Fig. 3.11. In the zigzag heterojunction, the valence band of MoSe$_2$ in the MoSe$_2$-TaS$_2$ heterostructure is $\sim 60$ meV below the Fermi level of TaS$_2$ for both strain configurations. The valence band of WSe$_2$ in the zigzag WSe$_2$-NbSe$_2$ heterostructure is 47 meV or 19 meV below the Fermi level of NbSe$_2$ as depending on the strain configuration.

The armchair heterostructures show negative Schottky barriers. The valence band of MoSe$_2$ is above the Fermi level for both strain configurations resulting in negative Schottky barriers. The barriers are 80 meV for MoSe$_2$ strained to TaS$_2$ and 42 meV for TaS$_2$ is strained to MoSe$_2$. The valence band of WSe$_2$ in the armchair WSe$_2$-NbSe$_2$ heterostructure is more sensitive to strain. Straining the WSe$_2$ to the NbSe$_2$ results in a positive Schottky barrier of 68 meV whereas straining the NbSe$_2$ to the WSe$_2$ gives a negative schottky barrier of 46 meV. Except for one strain configuration of the WSe$_2$-
Figure 3.12: Bond lengths (in Å) of (a) armchair and (b) zigzag interface of MoSe$_2$-TaS$_2$ lateral heterostructures. The strained interface bonds are circled in red.

One reason for the different barrier height for different interfaces could be the different strain associated with the armchair and zigzag interfaces. Fig. 3.12 shows the bond lengths of armchair and zigzag interfaces of the MoSe$_2$-TaS$_2$ heterostructures where MoSe$_2$ is strained to match the lattice constant of TaS$_2$. The initial bond lengths of Mo–Se and Ta–S were 2.48 Å, and after relaxation the Mo–Se bond lengths became $\sim$ 2.57 Å at the armchair interface and 2.56 Å at the zigzag interface and 2.55 Å away from the interface for both armchair and zigzag configuration. The bond lengths of Ta–S
became 2.47 Å at the interface and 2.48-2.50 Å away from the interface for armchair configuration. The bond lengths of Ta–S became 2.43 Å at the interface and 2.50-2.51 Å away from the interface for zigzag configuration. The Ta–S bond lengths are strained ~ 0.4% at the armchair interface and 2% at the zigzag interface. Thus, the strain in the interface Ta–S bonds is considerably higher at the zigzag interface than at the armchair interface. This difference in strain might be one mechanism that alters the energy level alignments.

Figure 3.13: Charge transfer at the (a) armchair and (b) zigzag interface of MoSe$_2$-TaS$_2$ lateral heterostructures.

It is also known that the energy levels of the edge states of TMDCs depend on the type of edge. The energetics are similar to those of graphene edges. Passivated armchair edges of MoS$_2$ are semiconducting with a smaller gap than that of the the bulk, and zigzag edges are always metallic with an edge state crossing the Fermi level within the bulk bandgap [115]. This metallic edge state could either pin or shift the Fermi level
into the gap in a zizag interface. Understanding the physical mechanisms governing the edge dependence of the band alignment is still an open line of investigation.

Fig. 3.13 illustrates the charge transfer in the armchair and zigzag interface of MoSe$_2$-TaS$_2$ lateral heterostructures. Yellow indicates electron surplus and the blue indicates electron deficiency. This indicates there is a charge transfer between the metal and semiconducting TMDCs, but it’s significance in terms of understanding the different offsets resulting from different interface is not clear.
Chapter 4

Conclusions

The electronic properties of the vertical and lateral metal-semiconductor TMDC heterostructure have been studied by first-principle calculations. To improve the contact resistance and to avoid FLP, we used m-TMDCs as contacts to s-TMDCs. In the MoSe$_2$-NbS$_2$, MoTe$_2$-TaSe$_2$, WSe$_2$-NbS$_2$, and WSe$_2$-TaS$_2$ vertical heterostructures, the VBM is less than 0.2 eV below the Fermi level. Our calculations highlight the ability to achieve interfaces with low valence band offsets between the semiconducting and metallic TMDCs. In the lateral metal-semiconductor TMDC heterostructures, the armchair MoSe$_2$-TaS$_2$ heterostructure in two strain condition and the armchair WSe$_2$-NbSe$_2$ heterostructure where the NbSe$_2$ is strained to WSe$_2$, have the VBM of the s-TMDCs lying above the Fermi level, creating a negative p-type Schottky barrier. A negative p-type Schottky barrier is desired for low resistance hole injection. Our calculations predict that the metal-semiconducting TMDCs vertical and lateral heterostructure could facilitate low-resistance p-type contacts with pristine interfaces to monolayer TMCDs.
Chapter 5

Future Plan

In the horizontal heterostructures, the potential in the direction perpendicular to the interfaces is that of a superlattice, since periodic boundary conditions are applied to the supercells. If the semiconducting regions are short enough, the metal states can tunnel through the semiconducting region and couple to the next metal region in the adjacent unit cells. When this happens, superlattice minibands form, and the energetic width of the miniband gives the strength of the coupling. The formation of minibands results in energy broadening of the metal states, and if this energy broadening is similar to the Fermi level alignment, then it puts the value of the alignment energy into question.

If we zoom in to the $\Gamma - X'$ path of the armchair configuration of MoSe$_2$-TaS$_2$, there is some dispersion to the bands as shown in Fig. 5.1(b). There are cosine minibands near the Fermi level with bandwidth of 50 meV. These bandwidths are of the same order as the band offsets. The energy broadening due to the mini bands may effect the calculated band offsets.

To clarify this, we will eliminate the coupling through the semiconducting region by increasing the length of the semiconductor region. We will simulate the lateral
Figure 5.1: Band structure of MoSe$_2$-TaS$_2$ (a) armchair configuration (b) zoomed $\Gamma - X'$ area of k-path, (c) zigzag configuration and (d) zoomed $X - \Gamma$ area of k-path.

heterostructure increasing length of the semiconducting region until the miniband width is a small fraction of the valence band offset. Once the miniband width is a small fraction of the band offset, we can rule out mini-band formation as the source of the negative Schottky barrier.
Bibliography


