Optimizing Charge Injection across Transition Metal Dichalcogenide Heterojunctions: Theory and Experiment

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Supporting Information

ABSTRACT: In search of an improved strategy to form low-resistance contacts to semiconducting transition metal dichalcogenides, we combine ab initio density functional electronic structure calculations for an NbSe2/WSe2 interface with quantum transport measurements of the corresponding heterojunction between a few-layer WSe2 semiconductor and a metallic NbSe2 layer. Our theoretical results suggest that, besides a rigid band shift associated with charge transfer, the presence of NbSe2 does not modify the electronic structure of WSe2. Since the two transition metal dichalcogenides are structurally similar and display only a small lattice mismatch, their heterojunction can efficiently transfer charge across the interface. These findings are supported by transport measurements for WSe2 field-effect transistors with NbSe2 contacts, which exhibit nearly ohmic behavior and phonon-limited mobility in the hole channel, indicating that the contacts to WSe2 are highly transparent.

KEYWORDS: transition metal dichalcogenides, contacts, heterojunctions, ab initio calculations, electronic structure

Since mechanically exfoliated ultrathin niobium diselenide (NbSe2) has displayed superconducting behavior and single-layer molybdenum disulphide (MoS2) has been identified as a direct-gap semiconductor and used in a field-effect transistor, the family of layered transition metal dichalcogenide (TMD) materials has attracted much attention as promising candidates for two-dimensional (2D) electronics and optoelectronics applications. Even though much effort has been spent to fabricate high-performance devices, the success has been limited by lack of a viable strategy to form low-resistance ohmic contacts between TMDs and electrodes. The local doping method used at silicon-metal interfaces in traditional three-dimensional (3D) Si devices can not be replicated in 2D systems. In TMDs contacted by a metal, carrier injection across the interface is typically limited by significant Schottky barriers. This effect can be partly mitigated by using metals with a work function close to the conduction band minimum (CBM) or valence band maximum (VBM), which lowers the Schottky barrier height (SBH) and thus decreases the contact resistance. Still, the complex Fermi level pinning at the electrode-semiconductor interface makes it even harder to achieve ohmic contacts. Other strategies to reduce the contact resistance, including attempts to fabricate in-layer junctions by phase engineering, 2D/2D interlayer junctions with weak Fermi level pinning, 28 use of doped graphene, 29–32 doped TMDs, 33 or inserting hexagonal boron nitride (hBN) at the metal-TMD interface, 34 have been met with mixed success.

Our choice of metallic TMDs as drain/source contacts is largely motivated by the successful demonstration of graphene as a contact material for achieving low-resistance contacts to semiconducting TMDs. However, the atomic thickness and rather low sheet carrier density in graphene also introduce a relatively high effective contact resistance comprised of the graphene sheet resistance and the graphene/metal contact resistance. A good strategy to further reduce the effective contact resistance in TMD field-effect transistors (FETs) is to replace graphene as contact material by 2D metallic TMDs with substantially lower sheet resistance and fewer interface states due to the lack of dangling bonds.

Here we propose to use metallic TMDs as drain/source contacts as an alternative to previous contacting strategies that may provide low-resistance contacts to semiconductor TMDs. We combine ab initio density functional electronic structure calculations for an NbSe2/WSe2 interface with quantum transport measurements of the corresponding heterojunction between a few-layer WSe2 semiconductor and a metallic NbSe2 layer. Our theoretical results suggest that, besides a small rigid band shift associated with charge transfer, the presence of...
NbSe₂ does not modify the electronic structure of WSe₂. Since the two transition metal dichalcogenides are structurally similar and display only a small lattice mismatch, their heterojunction gives rise to only a small tunnel barrier so that charge can be injected efficiently across the interface. These findings are supported by transport measurements for WSe₂ field-effect transistors (FETs) with NbSe₂ contacts and a graphite gate, which exhibit nearly ohmic behavior and phonon-limited mobility in the hole channel, indicating that the contacts to WSe₂ are highly transparent.

RESULTS AND DISCUSSION

We first optimized the bulk structure of NbSe₂ and WSe₂ in the stable 2H phase and show our results in Figure 2a,b. Results of our DFT-optB86b-vdW calculations show that the AB layer stacking is energetically favorable to the AA stacking in both systems. For bulk NbSe₂, we found that our calculated in-plane lattice constant \( a_{\text{in-plane}} = 3.46 \) Å lies close to the observed value\(^{38} \) \( a_{\text{exp}} = 3.44 \) Å. Similarly, the calculated out-of-plane lattice constant \( c_{\text{out-of-plane}} = 12.74 \) Å, extending over two interlayer distances, lies close to the observed value\(^{38} \) \( c_{\text{exp}} = 12.48 \) Å. For bulk WSe₂, we obtained very good agreement with the experiment\(^{39} \) between \( a_{\text{exp}} = 3.30 \) Å and \( a_{\text{out-of-plane}} = 3.28 \) Å for the in-layer lattice constant and \( c_{\text{exp}} = 13.10 \) Å for the out-of-plane lattice constant. We notice that the in-layer lattice constant of NbSe₂ is only 5% larger than that of WSe₂ in the bulk, suggesting the likelihood of epitaxial stacking especially in few-layer systems.

We also found the AB stacking sequence to be preferred for the 2H-NbSe₂/2H-WSe₂ bilayer, depicted in Figure 1. The bilayer forms a honeycomb lattice with 6 atoms per unit cell, 3 of which are in the NbSe₂ and the other 3 in the WSe₂ layer. As seen in Figure 2c, the optimum in-layer lattice constant \( a_{\text{in-layer}} = 3.37 \) Å lies in-between the values for the individual bulk components. Also, as seen in Figure 2d, the value \( a_{\text{out-of-plane}} = 6.41 \) Å for the optimum interlayer distance, lies in-between the corresponding values in bulk NbSe₂ and WSe₂. The binding energy of the two layers is 0.19 eV per unit cell, based on DFT-optB86b-vdW, indicates that the interlayer coupling is weak.

The parabola fits of energy differences \( \Delta E \), shown by the dashed lines in Figure 2, indicate harmonic behavior of the bulk and bilayer structures within \( \approx 10\% \) of the optimum lattice constant \( d \) or interlayer distance \( d \).

Electronic band structure results for the NbSe₂/WSe₂ bilayer and its monolayer components are shown in Figure 3. As seen in Figure 3a, the NbSe₂/WSe₂ bilayer is metallic. To interpret the band structure of the bilayer, we calculated separately the band structure of isolated NbSe₂ and WSe₂ monolayers and displayed it in Figure 3b. These results indicate that the NbSe₂ monolayer is metallic, whereas the WSe₂ monolayer is semiconducting with a direct gap of about 1.35 eV at the K point. Even though the absolute value of the band gap is typically underestimated in DFT calculations, the dispersion of individual bands is usually in good agreement with more accurate self-energy calculations. We found that individual bands in isolated NbSe₂ and WSe₂ monolayers in Figure 3b can be identified in the band structure of the bilayer. To prove this point, we superposed the band structure of the two constituents, shifting the bands of WSe₂ rigidly up by 0.293 eV in Figure 3b, and present the resulting band structure in Figure 3c, along with the bilayer result of Figure 3a. The agreement between the band structure of the bilayer and the superposition of monolayers is near-perfect, suggesting the applicability of a rigid-band model in this system. Our finding that there is nearly no band rehybridization, but only a minor band realignment at the interface of NbSe₂ and WSe₂ monolayers also holds for WSe₂ multilayers with a narrower and indirect band gap.

As mentioned earlier, NbSe₂ is compressed by \( < 3\% \) and WSe₂ stretched by \( < 3\% \) in the bilayer as a result of the difference between the lattice constants. We found that these modest structural changes have a negligible effect on the electronic band structure.

To better characterize the NbSe₂/WSe₂ interface, we calculated the charge density difference \( \Delta \rho = \rho_{\text{bilayer}} - \sum \rho_{\text{monolayers}} \) associated with the assembly of the bilayer from isolated monolayers using a supercell with the lattice constant \( c = 24.0 \) Å, about four times the interlayer distance. This charge density difference is visualized by contour plots in Figure 4a. We find that the charge redistribution is very small, with electrons transferring mainly from the WSe₂ layer to the NbSe₂ layer. To further elucidate the charge redistribution, we averaged the charge density difference in planes with \( z = \text{const.} \) that are parallel to the NbSe₂ and WSe₂ layers. The averaged quantity \( \langle \Delta \rho(z) \rangle \) shown by the solid line in Figure 4b, displays many oscillations even in individual TMD layers. To better understand the net charge flow, we convoluted the raw data by a Gaussian with a full-width at half-maximum of 0.17. The resulting function, displayed by the blue dashed line in Figure 4b, indicates a very small net flow of electrons from WSe₂ and the interface to the NbSe₂ layer. This result is consistent with the upward shift of WSe₂ bands discussed in relation to Figure 3c and also a previous report for the VS₂/MoS₂ bilayer system.\(^{28}\) As a more quantitative measure of the charge redistribution, we performed the Bader charge analysis\(^{40–45} \) in the NbSe₂/WSe₂ bilayer and found that 0.017 electrons per unit cell have been transferred from the WSe₂ to the NbSe₂ layer upon forming the interface.

Since charge injection across the interface is limited by potential energy barriers, which act as tunnel or Schottky barriers, we also investigated the local electrostatic potential \( V \) in the whole NbSe₂/WSe₂ interface region. To facilitate the interpretation, we averaged \( V \) in \( z = \text{const.} \) planes, similar to the way we averaged the charge density difference \( \Delta \rho(z) \) in
Figure 4b. The corresponding results for $\langle V(z/c) \rangle$ are presented in Figure 4c. The difference between the electrostatic potential in the vacuum region and at the Fermi level, given by $V_{\text{vacuum}} - E_F \approx 5.6 \text{ eV}$, corresponds to the work function. We also observe a narrow tunnel barrier characterized by $\Delta z \approx 1.8 \text{ Å}$ and $\Delta V \approx 4.5 \text{ eV}$ when measured from the Fermi level, resulting in a high tunneling probability across the interface, translating into high contact transparency.18

As a counterpart of the theoretical study, we have fabricated few-layer WSe$_2$ FETs with NbSe$_2$ drain/source contacts using van der Waals assembly. Our experimental results are summarized in Figure 5. Figure 5a illustrates schematically a few-layer WSe$_2$ FET with NbSe$_2$ drain and source contacts. The WSe$_2$ channel is placed on top of an hBN/graphite stack and is passivated by another hBN thin crystal from the top. Graphite is used as a gate electrode. These devices exhibit highly asymmetric ambipolar behavior with significantly higher hole than electron current, indicating that the Fermi level of NbSe$_2$ is aligned much closer with the VBM than the CBM of WSe$_2$. This is consistent with our band structure results for the...
NbSe₂/WSe₂ bilayer shown in Figure 3. As mentioned earlier, few-layer WSe₂ used in the experimental study has a narrower band gap than a monolayer and will incur a smaller rigid upshift of its bands.

Our observations suggest that we have achieved near-ohmic contacts for the hole channel. Variable temperature electrical measurements performed on WSe₂ FETs with NbSe₂ contacts reveal that as the temperature decreases from room temper-

Figure 4. (Color online) Electronic structure changes associated with assembling the NbSe₂/WSe₂ bilayer from isolated monolayers. (a) Charge density difference \( \Delta \rho \) is shown by isosurfaces bounding regions of electron excess at \(+2.5 \times 10^{-4} \) e/Å³ (yellow) and electron deficiency at \( -2.5 \times 10^{-4} \) e/Å³ (blue). \( \langle \Delta \rho (z/c) \rangle \) averaged across the \( x - y \) plane of the layers. The raw data, shown by the red solid line, and their convolution by a Gaussian with a full-width at half-maximum \( \Delta (z/c) = 0.17 \), shown by the blue dashed line. (c) Electrostatic potential \( \langle V(z/c) \rangle \) averaged across the \( x - y \) plane of the layers. \( z/c \) indicates the relative position of the plane within the unit cell with \( c = 24.0 \) Å.

Figure 5. (Color online) Design and characteristics of a few-layer WSe₂ FET with NbSe₂ contacts. (a) Schematic illustration of the WSe₂ device with NbSe₂ drain/source contacts and a graphite gate. The channel has been an encapsulated in hBN. (b) Room-temperature \( I_{ds} - V_g \) transfer characteristics of a WSe₂ FET exhibiting asymmetric ambipolar behavior with an on/off ratio of \( 10^7 \) for holes and \( 10^5 \) for electrons. The WSe₂ channel is \( \approx 5.5 \) nm thick, \( \approx 5.5 \) μm long, and \( \approx 2.6 \) μm wide. (c, d) Linearity of the \( I_{ds} - V_g \) output characteristics of the WSe₂ device. Room-temperature measurements for gate voltages ranging between \( V_g = -16 \) V and \( -6 \) V (c) are compared to measurements at \( V_g = -16 \) V in the temperature range from \( T = 77 \) to 295 K (d). Both sets of measurements indicate that contacts for the hole channel are near-ohmic. (e) Temperature-dependent two-terminal conductivity \( \sigma \) of the WSe₂ device as a function of gate voltage at \( V_{th} = -100 \) mV. (f) Two-terminal measurements of the field-effect hole mobility \( \mu_{FE} \) of the WSe₂ device as a function of temperature. Observed \( \mu_{FE} \) values increase from 106 to 283 cm²V⁻¹s⁻¹ as the temperature decreases from 295 to 77 K.
ature to 77 K, the extrinsic two-terminal field-effect mobility increases from \( \approx 107 \) to \( \approx 286 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \), indicating that the mobility of our NbSe\(_2\)-contacted WSe\(_2\) devices is limited by the phonons in the channel and not by the contacts.

The transfer curve of a typical hBN-encapsulated WSe\(_2\) FET with NbSe\(_2\) drain and source contacts and a graphite back gate is reproduced in Figure Sb. The few-layer WSe\(_2\) device is \( \approx 5.5 \) nm thick and exhibits a highly asymmetric ambipolar behavior, with an on/off ratio of 10\(^3\) for holes and of 10\(^3\) for electrons at a drain-source voltage of \(-1\) V. As shown in Figure S2 in the Supporting Information, the on-state hole current is about 2 orders of magnitude higher than in our few-layer WSe\(_2\) devices with conventional Ti/Au contacts, suggesting that 2D NbSe\(_2\) is superior to conventional 3D metals as a contact material.

A gate overdrive voltage, when applied to the device, is defined as \( V_{\text{Drive}} = |V_g - V_{\text{mid}}| \), where \( V_g \) is the applied gate voltage and \( V_{\text{mid}} \) is the gate voltage used to obtain the current minimum. Applicable bi-polarity values of gate overdrive voltages for electron and hole injection is expected to cause a similar degree of band bending. Consequently, observing a nearly 2 orders of magnitude higher on-current in the hole channel than in the electron channel suggests that the Fermi level of NbSe\(_2\) contacts is aligned much closer to the VBM than to the CBM of WSe\(_2\). We thus conclude that the tunnel or Schottky barrier height is much lower for the hole channel than for the electron channel.

Next, we focus on the hole channel of the device. As shown in Figure 5c, the output characteristics of the WSe\(_2\) device at room temperature are linear at all gate voltages between \( V_g = -16 \) V and \(-6\) V. Whereas a linear \( I_{\text{th}} - V_{\text{th}} \) characteristic usually indicates an ohmic contact, thermally assisted tunneling through a finite tunnel or Schottky barrier could also lead to linear response. To shed additional light on the quality of the NbSe\(_2\) contacts, we performed temperature dependent measurements and present them in Figure 5d. Indeed, these results show that the \( L_{\text{th}} - V_{\text{th}} \) curves remain linear down to \( T = 77 \) K at a gate voltage \( V_g = -16 \) V, providing further evidence that NbSe\(_2\) forms low-barrier and highly transparent contacts to the WSe\(_2\) channel for hole injection.

It is worth pointing out that the rigid upshift of WSe\(_2\) bands, predicted for the NbSe\(_2\)/WSe\(_2\) bilayer, is expected to be significantly reduced for NbSe\(_2\) in contact with few-layer WSe\(_2\) devices due to a more gradual charge redistribution and a smaller band gap in few-layer WSe\(_2\). Consequently, the band offset between WSe\(_2\) in the NbSe\(_2\)/WSe\(_2\) contact region and in the channel region will also be reduced. Consequently, the in-plane Schottky barrier between few-layer WSe\(_2\) interfacing NbSe\(_2\) in the contact region and the isolated WSe\(_2\) channel will be diminished, leading to the experimentally observed ohmic behavior in NbSe\(_2\)-contacted few-layer WSe\(_2\) devices.

To further demonstrate the high quality of the NbSe\(_2\) contacts, we reproduce in Figure 5e the two-terminal conductivity of the same WSe\(_2\) device at different temperatures. The two-terminal conductivity is defined by \( \sigma = I_{\text{th}}/V_{\text{th}} \times L/W, \) where \( L \) is the length and \( W \) the width of the channel. Similar to WSe\(_2\) FETs with graphene and 2D/2D contacts, which have been reported in our previous studies,\(^{29,33}\) the WSe\(_2\) channel with NbSe\(_2\) contacts also exhibits a metal–insulator transition (MIT). The on-state conductivity at \( V_g = -16 \) V increases monotonically by a factor of \( \approx 3 \) as the temperature decreases from \( T = 295 \) to 77 K.

Finally, we extracted the field-effect mobility from the linear region of the conductivity curves in the metallic state at \(-16 \) V < \( V_g < -10 \) V using the expression \( \mu_{\text{FE}} = (1/C_g) \times (dI/dV_g) \), where \( C_g \) is the geometric gate capacitance of a 40 nm thick hBN layer\(^{44}\) with \( \epsilon = 3.5 \). As shown in Figure 5f, the hole mobility for the WSe\(_2\) device increases from \( \approx 106 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) to \( \approx 283 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) as the temperature decreases from room temperature to 77 K, strongly suggesting that the hole transport in the device channel is limited by phonons and not by contacts.\(^{29,45−47}\) The two-terminal field-effect mobility in our NbSe\(_2\)-contacted WSe\(_2\) devices is significantly higher than what has been reported for few-layer WSe\(_2\) devices with platinum bottom contacts.\(^{24}\) The weaker-than-expected temperature dependence of the two-terminal field-effect mobility could be attributed to the presence of a finite contact resistance. The limiting effect of the contact resistance on the current starts playing an increasing role as the channel resistance decreases with decreasing temperature.

Our study indicates that Schottky/tunnel barriers between metallic and semiconducting TMDs are fundamentally different from conventional metal–semiconductor Schottky barriers for the following two important reasons. First, the formation of interface states is suppressed in TMD heterojunctions due to the lack of dangling bonds on TMD surfaces, similar to what is known about graphene/TMD junctions. Second, an abrupt potential drop, rather than a relatively thick depletion layer, forms across the “van der Waals gap” of TMD heterojunctions. As a result of these differences, Fermi level pinning is expected to be significantly reduced at the interface between metallic and semiconducting TMDs.

Our findings for optimizing contacts to WSe\(_2\) as channel material can be generally applied to also other TMD semiconductors, including MoS\(_2\), TcSe\(_2\), and TcTe\(_2\), which have been proposed for FETs applications.\(^{33,48}\) More recently, NbSe\(_2\) has also been used as a \( p \)-type contact to WSe\(_2\) but the contact quality and observed hole mobility were below our present results.\(^{49}\)

It is also worth pointing out that the relative crystalline orientation between the WSe\(_2\) channel and the NbSe\(_2\) contact layer has not been optimized and is random in our devices. Further improvement of the contact quality is expected by optimizing the stacking orientation in WSe\(_2\)/NbSe\(_2\) junctions.

**CONCLUSIONS**

In summary, we combined theoretical and experimental techniques to investigate an improved strategy to form ohmic low-resistance contacts to semiconducting TMDs. On the part of theory, we tested the potential merit of this approach using \textit{ab initio} density functional electronic structure calculations for an NbSe\(_2\)/WSe\(_2\) bilayer. Our theoretical results suggest that, besides a rigid band offset associated with a very small charge transfer, the presence of NbSe\(_2\) does not modify the electronic structure of WSe\(_2\). This basic finding remains valid also for multilayer systems. Since the two transition metal dichalcogenides are structurally similar and display only a small lattice mismatch, their heterojunction can efficiently transfer charge across the interface. These theoretical findings are supported by quantum transport measurements in a WSe\(_2\) field-effect transistor with NbSe\(_2\) contacts. We found that the hetero-junction between a few-layer WSe\(_2\) semiconductor and a metallic NbSe\(_2\) layer in this device exhibits nearly ohmic behavior and phonon-limited mobility in the hole channel, indicating that the contacts to WSe\(_2\) are highly transparent.
METHODS

Computational Techniques. We utilized ab initio density functional theory (DFT) as implemented in the VASP code\textsuperscript{50–52} to obtain the optimized structure and electronic properties of the TMD systems of interest. We have applied it to WSe\textsubscript{2} and NbSe\textsubscript{2} monolayers, the NbSe\textsubscript{2}/WSe\textsubscript{2} bilayer, and the corresponding bulk structures with AB stacking of layers. All 2D structures have been represented by a periodic array of slabs separated by a vacuum region in excess of 15 Å. We used projector-augmented-wave (PAW) pseudopotentials,\textsuperscript{53} the DFT-opt886-vdw\textsuperscript{54,55} exchange-correlation functionals. The Brillouin zone of the primitive unit cell of the 2D structures has been sampled by an \(8 \times 8 \times 1 \) k-point grid and that of bulk structures by an \(8 \times 8 \times 2 \) k-point grid.\textsuperscript{56} We used 500 eV as the electronic kinetic energy cutoff for the plane-wave basis and a total energy difference between subsequent self-consistency iterations below \(10^{-6} \) eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method,\textsuperscript{57} until none of the residual Hellmann–Feynman forces exceeded \(10^{-4} \) eV/Å.

Experimental Techniques. We fabricated WSe\textsubscript{2} FETs with NbSe\textsubscript{2} drain/source contacts by mechanical exfoliation and van der Waals assembly of WSe\textsubscript{2} and NbSe\textsubscript{2} crystals using polydimethylsiloxane (PDMS) stamps as schematically shown in Figure 5a. The WSe\textsubscript{2} channel with NbSe\textsubscript{2} drain/source contacts has been placed onto a hBN/graphite stack previously assembled on a SiO\textsubscript{2} substrate and electronic kinetic energy cutoff for the plane-wave basis and a total energy difference between subsequent self-consistency iterations below \(10^{-6} \) eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method,\textsuperscript{57} until none of the residual Hellmann–Feynman forces exceeded \(10^{-4} \) eV/Å.

Excess of 15 Å. We used projector-augmented-wave (PAW) structures with AB stacking of layers. All 2D structures have been sampled by an \(8 \times 8 \times 1 \) k-point grid and that of bulk structures by an \(8 \times 8 \times 2 \) k-point grid.\textsuperscript{56} We used 500 eV as the electronic kinetic energy cutoff for the plane-wave basis and a total energy difference between subsequent self-consistency iterations below \(10^{-6} \) eV as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method,\textsuperscript{57} until none of the residual Hellmann–Feynman forces exceeded \(10^{-4} \) eV/Å.

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REFERENCES


