First-principles simulation of monolayer hydrogen passivated Bi$_2$O$_2$S$_2$–metal interfaces†

Linliang Xu,†,a Shiqi Liu,†,b c Han Zhang,† Xiuying Zhang,† Jingzhen Li,† a Jiahuan Yan,† b Bowen Shi,† a Jie Yang,† Chen Yang,† ab Lianliang Xu, c Xiaotian Sun,‡ a and Jing Lu∗aef

Monolayer (ML) MoS$_2$ is one of the most extensively studied two-dimensional (2D) semiconductors. However, it suffers from low carrier mobility and pervasive Schottky contact with metal electrodes. 2D semiconductor Bi$_2$O$_2$S$_2$, a sulfur analogue of 2D Bi$_2$O$_2$Se, has been prepared recently. ML fully hydrogen-passivated Bi$_2$O$_2$S$_2$ (Bi$_2$O$_2$S$_2$H$_2$) possesses a comparable band gap (1.92 eV) with ML MoS$_2$ (1.8 eV), but probably has a better device performance than ML MoS$_2$. Based on the density functional theory, the electron and hole mobilities of ML Bi$_2$O$_2$S$_2$H$_2$ at 300 K are calculated to be 16447–26699 and 264–968 cm$^2$/V·s, respectively. Then we firstly characterize the contact properties of ML half-hydrogen-passivated Bi$_2$O$_2$S$_2$ (Bi$_2$O$_2$S$_2$H) with four bulk metal electrodes (Ti, Sc, Pd, and Pt) based on ab initio quantum transport simulation. In the lateral direction, a p-type Schottky contact is found in Pd and Pt electrodes, and the corresponding hole Schottky barrier heights (SBHs) are 0.54 and 0.99 eV, respectively. Remarkably, a coveted n-type Ohmic contact appears in Sc and Ti electrodes. Finally, the current on–off ratio of the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ field effect transistor with a Ti electrode reaches 10$^{5}$. Hence, the good intrinsic properties, contact properties, and large switching ability put ML hydrogen-passivated Bi$_2$O$_2$S$_2$ in the rank of potential channel candidates for post-silicon era field effect transistors.

Introduction

Two-dimensional (2D) semiconductors such as transition metal dichalcogenides (TMDs),1–5 phosphorene,6–8 antimonene,9,10 and indium selenide (InSe)11,12 have aroused extensive attention. They are anticipated to be prospective channel material candidates for next-generation electronics as a result of their excellent gate electrostatics owing to their atomic-scale thickness and efficient carrier transport due to the smooth surface and few dangling bonds in the interface.3,13,14 MoS$_2$ is the most extensively studied 2D TMD. It has an appropriate band gap (1.8 eV), but the carrier mobility (200 cm$^2$/V·s) is obviously low, rendering it unsuitable for high-performance devices.2,4,15 2D InSe and phosphorene have a suitable band gap (0.69–1.52 eV for InSe and 0.3–1.0 eV for phosphorene, respectively) and a relatively high carrier mobility (~10$^3$ cm$^2$/V·s$^{-1}$), but are air sensitive.6–8,16–23 A 2D semiconductor with both air stability and high carrier mobility is elusive. Recently, a novel 2D ultrathin Bi$_2$O$_2$Se semiconductor has been fabricated.24,25 It has a high electron mobility of over 2000 cm$^2$/V·s at room temperature and a high on-off ratio of over 10$^6$. Besides, 2D Bi$_2$O$_2$Se is stable in air.25 Thin-film Bi$_2$O$_2$S, a sulfur analogue of Bi$_2$O$_2$Se, with a moderate band gap (1.12–1.5 eV) and air stability also has been successfully synthesized.26–28 In view of the similarity with Bi$_2$O$_2$Se, Bi$_2$O$_2$S is expected to possess a high carrier mobility and on-off ratio as well. Herein, these advantages make 2D Bi$_2$O$_2$S a 2D potential channel candidate for post-silicon era field effect transistors.

In a real field effect transistor (FET) with a 2D semiconductor as the channel, a sustainable and controllable substitutional doping scheme is always lacking. Hence, a metal electrode is generally required to be in direct contact with the 2D channel for injecting appropriate types of carriers.29,30 The metal-semiconductor contact is often related to the generation of the Schottky barrier, which suppresses the injection of the carrier.31–33

Unfortunately, the Schottky barrier heights (SBHs) are usually influenced by Fermi level pinning (FLP), which...
structure, we take both the top and bottom S\(_2\)Bi\(_2\)O\(_2\)S and bulk metal remains lacking.

In this article, monolayer (ML) fully hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) (Bi\(_2\)O\(_2\)S\(_2\)H\(_2\)) is used in our calculations. Since the (Bi\(_2\)O\(_2\)S\(_2\))\(^+\) cationic layer and S\(^2-\) anionic layer appear alternately in a 2D Bi\(_2\)O\(_2\)S structure, we take both the top and bottom S\(^2-\) anionic layer into account. In order to eliminate the electronegative effects of the Bi\(_2\)O\(_2\)S\(_2\) structure, the hydrogen atoms are adopted to passivate the outermost S\(^2-\) anionic layer. We calculate the carrier mobility of ML Bi\(_2\)O\(_2\)S\(_2\)H\(_2\) according to the deformation potential theory. The result shows that ML Bi\(_2\)O\(_2\)S\(_2\)H\(_2\) has an electron mobility of 26 699 and 16 447 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the x and y directions, respectively, while it possesses a hole mobility of 264 and 968 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the x and y directions, respectively. Then the contact characteristics of ML half hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) (Bi\(_2\)O\(_2\)S\(_2\)H) with four metal electrodes (Ti, Sc, Pd, and Pt) are investigated based on the density functional theory and quantum transport simulation (QTS). In the vertical direction, the ML Bi\(_2\)O\(_2\)S\(_2\)H band structure is hybridized, resulting in the absence of a Schottky barrier. In the lateral direction, the quantum transport simulation suggests a p-type Schottky contact at the ML hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\)–Pd/Pt systems because of the normal FLP, which could be attributed to the MIGS and characterized by an average pinning factor S of 0.21. The corresponding hole SBHs for Pd/Pt are 0.54/0.99 eV. By contrast, an abnormal FLP of ML hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) appears for Ti and Sc electrodes owing to the dipole induced by charge redistribution at the interface between metallized ML Bi\(_2\)O\(_2\)S\(_2\)H and channel ML Bi\(_2\)O\(_2\)S\(_2\)H\(_2\). Consequently, a lateral n-type Ohmic contact is shaped. In the end, the ML hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) FET with the Ti electrode shows a current on-off ratio of 10\(^5\) and a subthreshold swing (SS) of 270 mV dec\(^{-1}\). Hence, excellent intrinsic properties can be found for the ML Bi\(_2\)O\(_2\)S\(_2\)H and a high-performance ML hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) FET is capable of being achieved.

**Methodology**

We perform the geometric optimization and electronic structure calculation using the Vienna ab initio simulation package (VASP).\(^{35-37}\) The projector-augmented wave (PAW) pseudopotential\(^{38,39}\) and plane wave basis set with a cutoff energy of 400 eV are adopted. For all these composite systems, the Monkhorst–Pack k-point meshes are sampled with a mesh of 0.02 and 0.07 Å\(^{-1}\) in the Brillouin zone for the electronic structure calculations and geometry optimization, respectively. To obtain a reliable geometric structure, we adopt the convergence with the energy underneath 10\(^{-6}\) eV and the force on each atom less than 0.02 eV Å\(^{-1}\). On the other hand, two corrections are taken into account to obtain more accurate consequence: the DFT-D3 for considering the van der Waals (vdW) interaction\(^{40}\) and the dipole correction for eliminating the artificial interaction between charged supercells due to the periodic boundary condition in the z-direction.\(^{41,42}\) More than 15 Å vacuum buffer space is set along the z-axis for avoiding pseudo interactions among the neighboring slabs.

The ML hydrogen-passivated Bi\(_2\)O\(_2\)S\(_2\) transistor is constructed with a two-terminal model, where the 5 nm ML Bi\(_2\)O\(_2\)S\(_2\)H\(_2\) and the optimized ML Bi\(_2\)O\(_2\)S\(_2\)H–metal interfaces are considered as the channel and the electrodes (Fig. 6), respectively. We calculate the transport properties by using the non-equilibrium Green’s function (NEGF) method coupled with density functional theory (DFT), which is implemented in the Atomistix ToolKit (ATK) 2019 package.\(^{43-45}\) The transmission coefficient \(T^k(E)\) is defined as:

\[
T^k(E) = \text{Tr}\left[ \Gamma^k L(E) G^k(E) \Gamma^k R(E) G^k(E) \right]
\]

here, \(k\) stands for the reciprocal lattice vector point along a surface-parallel direction (orthogonal to the transmission direction) in the irreducible Brillouin zone (IBZ). The gamma function \(\Gamma^k_{L/R} = \frac{\sum_{k}^{\infty}}{\sum_{k}^{\infty}}\) stands for the level broadening because of the right (left) electrode expressed by the way of the electrode self-energies \(\Sigma^k_{L/R}\), which is a description of the influence of the electrodes on the scattering region. \(G^{k\dagger} (G^k)\) represents the advanced (retarded) Green’s function. The transmission parameter \(T(E)\) is the average of the transmission coefficient \(T^k(E)\) \(k\) is taken through the IBZ. A single-\(z\) polarized (SZP) basis set is used for obtaining enough accurateness.

The temperature and the real-space mesh cutoff are set at 300 K and 75 Hartree, respectively. Monkhorst–Pack k-point meshes of 50 × 1 × 25 and 50 × 1 × 25 are employed for simulating the electronic structures of the electrodes and the central region, respectively. The x, y, and z directions of the FET (Fig. 6) adopt the periodic, Neumann, and Dirichlet type boundary conditions, respectively. In addition, the Perdew–Burke–Ernzerhof (PBE) form in the generalized gradient approximation (GGA) is applied in all the calculations.\(^{46}\)

Since the metal electrodes dope the 2D semiconductor channel, many-body effects have been greatly depressed, and thus the single electron approximation can effectively depict the electron behavior in a FET configuration.\(^{57,48}\) For instance, the DFT-GGA shows that the degenerately doped ML MoSe\(_2\) has a band gap of 1.52 eV, while the GW method and experiments give a band gap of 1.59 eV and 1.58 eV, respectively.\(^{49}\) The simulated transport gaps of ML bilayer (BL)/trilayer (TL) black phosphorene (BP) for the Ni electrode based on the DFT-GGA method are 0.79/0.81/0.68 eV,\(^{34,50,51}\) and the corresponding experimental values of the transport gaps are 0.99/0.71/0.61 eV.\(^{52}\)

**Results**

**Models**

In a bulk Bi\(_2\)O\(_2\)S structure, the (Bi\(_2\)O\(_3\))\(^2+\) cationic layers and the S\(^2-\) anionic layers appear alternately. Whether the top S\(^2-\) anionic layer or the bottom S\(^2-\) anionic layer belongs to ML Bi\(_2\)O\(_2\)S is unknown. Therefore, we take both the top S\(^2-\) anonic
layer and the bottom $S^{2-}$ anionic layer into account. However, the whole structure is electronegative. In order to maintain electric neutrality, we use the hydrogen atoms to passivate the outermost $S^{2-}$ anionic layer. Thus, the real stoichiometry of pristine ML Bi$_2$O$_2$S in our calculation is ML Bi$_2$O$_2$S$_2$H$_2$, including the free-standing ML Bi$_2$O$_2$S$_2$H$_2$ (Fig. 1(a)–(c)) and the Bi$_2$O$_2$S$_2$H$_2$ channels. This operation has been adopted in both ML Bi$_2$O$_2$Se and BL Bi$_2$O$_2$Se.41,42 Without including the spin–orbital coupling, the band structures of ML Bi$_2$O$_2$S$_2$ and ML Bi$_2$O$_2$S$_2$H$_2$ are calculated for comparison, as shown in Fig. S1 (ESI†) and Fig. 1(e), respectively. The result shows that ML Bi$_2$O$_2$S$_2$ is a conductor, while ML Bi$_2$O$_2$S$_2$H$_2$ is a semiconductor with an indirect band gap of 1.92 eV. The calculated lattice parameters of ML Bi$_2$O$_2$S$_2$H$_2$ are $a = 3.90$ Å and $b = 3.90$ Å, which agree well with previously reported results.26

The mobility $\mu$ is calculated according to the deformation potential theory proposed by Bardeen and Shockley.23 In a 2D material, $\mu$ is defined as:$$\mu = \frac{e\hbar C^{2D}}{k_B T m^* E_1}$$

where $e$, $\hbar$, and $k_B$ are the electron charge, Planck constant, and Boltzmann constant, respectively. The temperature $T$ is 300 K. $m^*$ is the electron (hole) effective mass along the transport direction. and $m_d$ is the mean carrier effective mass and can be calculated by the formula $m_d = \sqrt{m^* m^*_i}$, where $m^*_i$ and $m^*_e$ represent the effective mass along the $x$ and $y$ directions, respectively. The $C^{2D}$ stands for the elastic modulus for the 2D material and is calculated as $C^{2D} = \frac{2\nu E_0}{(1-\nu)(1-2\nu)}$, where $E_0$, $\nu$, and $l_0$ are the total energy, lattice volume at equilibrium state, lattice parameter, and the deformation of $l_0$, respectively. $\Delta l$ is taken from 0 to 2% with a step of 0.5%. The deformation potential $E_1$ is defined by $E_1 = \Delta E/\Delta l/l_0$, where $\Delta E$ is the energy change of the CBM or VBM under proper cell dilatation and compression. The calculated data for ML Bi$_2$O$_2$S$_2$H$_2$ are shown in Table 1. In the $x$ direction, ML Bi$_2$O$_2$S$_2$H$_2$ has an electron and hole mobility of 26.699 and 264 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. In the $y$ direction, the electron mobility of ML Bi$_2$O$_2$S$_2$H$_2$ decreases to the value of 16.447 cm$^2$ V$^{-1}$ s$^{-1}$ when compared to that in the $x$ direction, while the hole mobility of ML Bi$_2$O$_2$S$_2$H$_2$ increases to the value of 968 cm$^2$ V$^{-1}$ s$^{-1}$ when compared to that in the $x$ direction.

We choose four metals (Ti, Sc, Pd, and Pt) as electrodes to construct the interface between ML Bi$_2$O$_2$S$_2$H$_2$ and the metal. For simulating the bulk metal, the interfacial system contains five-layer metal atoms according to the previous studies.57–59 We set free the top three layers and fix the bottom two layers. The hydrogen atoms at the interface between ML Bi$_2$O$_2$S$_2$H$_2$ and the metal atoms are removed. This can be explained from two aspects. On the one hand, the hydrogen atoms at the interface interact strongly with the metal atoms, which leads to a strong deformation of the interfacial structure and make it hard to obtain a stable structure. On the other hand, removing the hydrogen atoms at the interface does not influence the coupling between the ML Bi$_2$O$_2$S$_2$H$_2$ and the metal. This is also demonstrated by the quick optimization of the interfacial structure to a stable configuration. Thus, the real stoichiometry of ML Bi$_2$O$_2$S$_2$H$_2$ used in the interfacial structure is ML Bi$_2$O$_2$S$_2$H. Both ML Bi$_2$O$_2$S$_2$H and the metal are stretched in our simulation and the lattice constant mismatches in these

### Table 1: Calculated carrier mobility. $m^*$, $E_1$, $C^{2D}$, and $\mu$ represent the deformation potential, elastic modulus, effective mass, and mobility for electrons ($e$) and holes ($h$) along the $x$ and $y$ directions in ML Bi$_2$O$_2$S$_2$H$_2$ at 300 K, respectively.

<table>
<thead>
<tr>
<th>Carrier type</th>
<th>$m^*$ ($m_e$)</th>
<th>$E_1$ (eV)</th>
<th>$C^{2D}$ (J m$^{-2}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$ ($x$)</td>
<td>0.15</td>
<td>$-1.896$</td>
<td>101.23</td>
<td>26.699</td>
</tr>
<tr>
<td>$h$ ($x$)</td>
<td>1.38</td>
<td>2.42</td>
<td>101.23</td>
<td>264</td>
</tr>
<tr>
<td>$e$ ($y$)</td>
<td>0.15</td>
<td>$-2.072$</td>
<td>101.59</td>
<td>16.447</td>
</tr>
<tr>
<td>$h$ ($y$)</td>
<td>1.38</td>
<td>$-1.084$</td>
<td>101.59</td>
<td>968</td>
</tr>
</tbody>
</table>

Fig. 1: (a) Top, (b) side, and (c) front view of the pristine ML Bi$_2$O$_2$S$_2$H$_2$. The primitive cell is represented by the red shadow. (d) Original configuration of the metal–ML Bi$_2$O$_2$S$_2$H interface. The different atoms are represented by the different color balls. (e) Band structure of the intrinsic ML Bi$_2$O$_2$S$_2$H$_2$. (f) DOS of the intrinsic ML Bi$_2$O$_2$S$_2$H$_2$. 


Table 2 Calculated interfacial properties of the ML Bi₂O₂S₂H–metal contacts. ε represents the average lattice constant mismatch of the metal–ML Bi₂O₂S₂H interface. \( d_z \) represents the average distance of the metal–ML Bi₂O₂S₂H interface in the vertical direction. \( d_{S-M} \) represents the minimum atom-to-atom distance from the metal atoms to sulfur atoms. \( E_b \) represents the energy per bismuth oxysulfide unit (Bi₂O₂S₂H) required to remove ML Bi₂O₂S₂H from the metal surface. \( W_{M-S} \) represents the calculated work function of the free-standing metal. \( \Phi_{L,W}^{M} \) represents the calculated work function of the ML Bi₂O₂S₂H–metal interface. \( \Phi_{L,T}^{M} \) represents the calculated work function of the ML Bi₂O₂S₂H–metal interface. 

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ti</th>
<th>Sc</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon (% )</td>
<td>2.47</td>
<td>1.03</td>
<td>2.18</td>
<td>2.25</td>
</tr>
<tr>
<td>( d_z (\text{Å}) )</td>
<td>1.71</td>
<td>1.84</td>
<td>1.85</td>
<td>1.97</td>
</tr>
<tr>
<td>( d_{S-M} (\text{Å}) )</td>
<td>2.46</td>
<td>2.50</td>
<td>2.27</td>
<td>2.28</td>
</tr>
<tr>
<td>( E_b (\text{eV}) )</td>
<td>4.74</td>
<td>4.63</td>
<td>3.29</td>
<td>2.67</td>
</tr>
<tr>
<td>( W_{M-S}(\text{eV}) )</td>
<td>4.32</td>
<td>3.56</td>
<td>5.15</td>
<td>5.65</td>
</tr>
<tr>
<td>( \Phi_{L,W}^{M}(\text{eV}) )</td>
<td>1.48</td>
<td>1.39</td>
<td>2.22</td>
<td>4.00</td>
</tr>
<tr>
<td>( \Phi_{L,T}^{M}(\text{eV}) )</td>
<td>0.06</td>
<td>0.55</td>
<td>-0.28</td>
<td>-2.06</td>
</tr>
<tr>
<td>( \Phi_{L,T}^{M}(\text{eV}) )</td>
<td>-0.24</td>
<td>-0.15</td>
<td>1.51</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Three initial interfacial stacking configurations are considered in our calculation. In the first configuration, the metal atoms sit above the Bi or O atoms. In the second configuration, the metal atoms sit above the center between the Bi and O atoms. In the third configuration, some metal atoms sit above the Bi or O atoms, and some metal atoms sit above the center between the Bi and O atoms. The size of the supercells used in the different calculations is shown as follows. The \( 2 \times \sqrt{3} \) unit cell of Ti is adjusted to the \( \sqrt{2} \times \sqrt{2} \) unit cell of ML Bi₂O₂S₂H. The \( \sqrt{5} \times \sqrt{13} \) unit cell of Sc is adjusted to the \( \sqrt{2} \times 3 \) unit cell of ML Bi₂O₂S₂H. The \( 3 \times 3 \) unit cell of Pd and Pt is adjusted to the \( 2 \times \sqrt{5} \) unit cell of ML Bi₂O₂S₂H.

For the Ti electrode, the result shows that all the metal atoms sit above the Bi or O atoms after optimization for the three initial interfacial stacking configurations, as shown in Fig. S2 (ESI†). For Sc and Pd electrodes, all the metal atoms tend to choose the third stacking configuration after optimization for the three initial stacking configurations (see Fig. S3 and S4, ESI†). As displayed in Fig. S5 (ESI†), the second stacking configuration for the Pt electrode forms an unstable structure after optimization. Thus, only the first and third stacking configurations are considered, which tend to choose the third stacking configuration after optimization. Therefore, different stacking modes for the four metals are consistent with each other in our calculation.

Electronic structure calculation

Fig. 2 displays the optimized structures of the ML Bi₂O₂S₂H–metal interfaces. When ML Bi₂O₂S₂H is in contact with the Ti/Sc/Pd/Pt electrode, its structure is almost kept intact. Table 2 presents the main parameters of the ML Bi₂O₂S₂H–metal interfaces. \( d_z \) is the mean distance between ML Bi₂O₂S₂H and the closest metal layer along the vertical direction, and \( d_{S-M} \) is the minimum distance from the sulfur atom to the metal atoms. \( W_{M-S} \) is the calculated work function of the ML Bi₂O₂S₂H–metal interface and is obtained from the average electrostatic potential distributions (see Fig. 2). The maximal electrostatic potential can be considered as the vacuum level.

Fig. 2 Side view of the relaxed structures and average electrostatic potential distributions in planes perpendicular to the ML Bi₂O₂S₂H–Ti/Sc/Pd/Pt interface. The corresponding atoms are shown on the right. The blue dashed lines denote the Fermi level.
Since the Fermi level is set at zero, the value of the maximal electrostatic potential is also the value of $W_{M-S}$. We define the binding energy $E_b$ of the metal–ML Bi$_2$O$_2$S$_2$H interface as:

$$E_b = (E_{Bi_2O_2S} + E_M - E_{Bi_2O_2S-M})/N$$

where, $E_M$, $E_{Bi_2O_2S}$, and $E_{Bi_2O_2S-M}$ stand for the total energy of the metal, the free-standing ML Bi$_2$O$_2$S$_2$H, and the ML Bi$_2$O$_2$S$_2$H–metal systems, respectively, and $N$ represents the total number of primitive cells (Fig. 1(a)) in the ML Bi$_2$O$_2$S$_2$H–metal interfaces.

Based on $E_b$ and $d_z$, two types of interactions between ML Bi$_2$O$_2$S$_2$H and metals are classified. The first is the strong interaction for Sc and Ti electrodes with a larger $E_b$ (4.63/4.74 eV for Sc/Ti) and a smaller $d_z$ (1.84/1.71 Å for Sc/Ti). The second is the relatively weak interaction for Pd and Pt electrodes with a smaller $E_b$ (3.29/2.67 eV for Pd/Pt) and a larger $d_z$ (1.85/1.97 Å for Pd/Pt).

The different numbers of the covalent bonds at the ML Bi$_2$O$_2$S$_2$H–metal interface result in different interaction intensities. The more the number of covalent bonds, the stronger the interaction intensity. One, two, zero, and two unpaired electrons exist in the outer orbits of the free-standing Sc (3d$^{1}$4s$^{2}$), Ti (3d$^{2}$4s$^{2}$), Pd (4d$^{10}$), and Pt (5d$^{5}$6s$^{1}$) atoms, respectively. Thus, Sc/Ti/Pd/Pt can form one/two/zero/two covalent bonds. However, after being in contact with ML Bi$_2$O$_2$S$_2$H, the $n$–d and $(n + 1)$–s electrons of Sc/Ti/Pd/Pt atoms undergo redistribution due to the orbital overlap according to the Mulliken population analysis. Herein, the real electronic configurations of Sc, Ti, and Pd are approximately 3d$^{4}$s$^{1}$, 3d$^{4}$s$^{1}$, and 4d$^{5}$s$^{1}$, respectively. Three/four covalent bonds are actually formed between Sc/Ti and ML Bi$_2$O$_2$S$_2$H, while two covalent bonds are actually formed between Pd/Pt and ML Bi$_2$O$_2$S$_2$H. Therefore, Sc and Ti atoms show a stronger interaction with ML Bi$_2$O$_2$S$_2$H than that with Pd and Pt atoms.

Fig. 3 displays the band structures of the ML Bi$_2$O$_2$S$_2$H–metal interfaces. The red line denotes the contribution from the ML Bi$_2$O$_2$S$_2$H. ML Bi$_2$O$_2$S$_2$H undergoes metallization, and no vertical Schottky barriers are formed in the four interfacial systems. The hybridization of the ML Bi$_2$O$_2$S$_2$H band structure suggests the formation of a covalent interaction at the four interfacial systems, and this agrees with the binding strength.

The partial density of states (PDOS) of ML Bi$_2$O$_2$S$_2$H–metal systems projected on ML Bi$_2$O$_2$S$_2$H are also calculated (Fig. 4). P states are the main component around the Fermi level, which is consistent with the outermost electronic configuration of Bi (6p$^3$), O (2s$^2$2p$^4$) and S (3s$^2$3p$^4$). The band gap of ML Bi$_2$O$_2$S$_2$H disappears in the four metal–ML Bi$_2$O$_2$S$_2$H interfaces because of the hybridization of ML Bi$_2$O$_2$S$_2$H. To further illustrate the interaction at the ML Bi$_2$O$_2$S$_2$H–metal interface, we also plot the total electron density distribution, as shown in Fig. 5. Apparently, plenty of electrons exist at the ML Bi$_2$O$_2$S$_2$H–metal interface, suggesting the strong covalent interactions.

**SBH of the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ transistors**

Fig. 6 displays the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET schematic diagram. The Schottky barrier increases the scattering of the carriers and decreases the performance of a FET. A ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET probably has two types of Schottky barrier at two interfaces: a vertical Schottky barrier ($\Phi_V$) exists in interface A and a lateral Schottky barrier ($\Phi_L$)
exists in interface B. According to our former analysis, the band structures of ML Bi₂O₂S₂H on the four metals are all metallized. The metallization of ML Bi₂O₂S₂H indicates no vertical Schottky barrier at interface A. Thus, only the lateral SBH needs to be paid attention.

Two common methods are used to obtain the lateral SBH $\Phi_L$, the QTS and the work function approximation (WFA). In the WFA, the lateral electron (hole) SBH $\Phi_{e/h}^{L,W}$ is defined as the difference between the CBM/VBM of free-standing ML Bi₂O₂S₂H₂ and the Fermi level of ML Bi₂O₂S₂H-metal composite electrode systems. We calculate the difference before the ML Bi₂O₂S₂H₂ channel contacts with the composite electrode. Therefore, the coupling between the channel and the composite electrode is neglected in the WFA approach. This method has been adopted in a previous study. Table 2 and Fig. 8 shows the corresponding results of the lateral SBH obtained by the WFA approach. The Ti/Sc electrode shows a lateral p-type Schottky contact with ML hydrogen-passivated Bi₂O₂S₂ with a hole SBH of 0.46/0.55 eV, while the Pd/Pt electrode shows a lateral p-type Ohmic contact with ML hydrogen-passivated Bi₂O₂S₂.

We obtain the lateral SBH $\Phi_L$ at the QTS level from the LDDOS of the ML hydrogen-passivated Bi₂O₂S₂ transistors by comparing the CBM/VBM of the ML Bi₂O₂S₂H₂ channel and the Fermi level at interface B. Because QTS takes the channel-electrode coupling into account, it is a more reliable way than WFA to determine the lateral SBH value. The values of the lateral SBH are averaged on the right and left interfaces due to the asymmetry of the FET structure. The ML, BL, and TL black phosphorus transistors with Ni electrodes have adopted this operation. As shown in Table 2 and Fig. 8, we compare the lateral SBHs attained from the QTS and WFA approaches. For Ti and Sc electrodes, these two approaches give opposite contact polarities.
The QTS shows an n-type Ohmic contact, while the WFA shows a p-type Schottky contact. The big difference between the two approaches originates from the Fermi level modulation of the metal–ML Bi$_2$O$_2$S$_2$H$_2$ composite systems induced by the dipole electric field at the interface.

In the right part of Fig. 9, we depict the Fermi level change from the clean metal to the metal–ML Bi$_2$O$_2$S$_2$H composite system and then to a ML hydrogen-passivated Bi$_2$O$_2$S$_2$ device. When the clean metal is in contact with ML Bi$_2$O$_2$S$_2$H directly, the Fermi level of the composite electrode goes through the first change. The Fermi level is reduced for Ti, Sc, and Pt electrodes, while it is almost unchanged for the Pd electrode. Then in a ML hydrogen-passivated Bi$_2$O$_2$S$_2$ device, the composite electrode is in contact with the ML Bi$_2$O$_2$S$_2$H$_2$ channel. In the WFA method, the coupling between the composite electrode and channel is not considered at all. Thus, only the first change of the Fermi level is included in the WFA approach when calculating the lateral SBH. By contrast, the QTS takes the coupling into account, which causes two effects on the Fermi level (this is the second change of the Fermi level). One effect is the Fermi level modulation of the metal–ML hydrogen-passivated Bi$_2$O$_2$S$_2$ composite systems. Indeed, the charge repulsion at the electrode-channel interface induces a charge redistribution and then generates a dipole electric field. The formation of the dipole electric field results in an abnormal FLP and thus modulates the Fermi level of the composite system. In the Ti/Sc-ML hydrogen-passivated Bi$_2$O$_2$S$_2$ systems, the Fermi levels are elevated to the conduction band of ML Bi$_2$O$_2$S$_2$H$_2$ and a desirable n-type Ohmic contact is formed. The same Fermi level modulation was also found in the Sc/Ti/Pt-ML Bi$_2$O$_2$Se systems. Other studies also have confirmed the existence of the Fermi level modulation in the metal–graphene and metal–MoS$_2$ interfaces.

The other effect is the formation of MIGS at the electrode-channel interface, which leads to a normal FLP. The QTS method inclines to form a Schottky contact due to the normal FLP, while the WFA method inclines to form an Ohmic contact. For the Pd/Pt electrode, the discrepancy between the two methods can be attributed to the normal FLP at the electrode-channel interface. As displayed in Fig. 7, there are plenty of MIGS at the interface for Pd and Pt electrodes, which leads to a strong normal FLP.

To further illustrate the normal FLP, we calculate the pinning factor $S$. $S$ describes the intensity of normal FLP, in which $S = 1$ and $S = 0$ indicate no FLP and full FLP, respectively. The Schottky–Bardeen model is adopted to calculate $S$. We should point out that there is no normal FLP in the Ohmic contacts based on the Schottky–Bardeen model. Thus, only the pinning factor $S$ of Pd and Pt electrodes is calculated. $S$ is defined as:

$$S = \left(1 + \frac{e^2 N_0}{\epsilon_0} \alpha \right)^{-1}$$

where $\epsilon_0$, $e$, $\alpha$, and $N_0$ are the vacuum dielectric constant, the electron charge, the decay length of the MIGS, and the density of interfacial electronic states around the Fermi level per area, respectively. We use the integral $N_0 = \int_{E_f}^b n(E) dz$ ($a$ and $b$ are the boundary of the MIGS area around the Fermi level) to calculate $N_0$. $n(E)$ is the density of states at the interface around

**Fig. 9** (a) Comparison of the energy level between ML hydrogen-passivated Bi$_2$O$_2$S$_2$ and Bi$_2$O$_2$Se$_2$ when in contact with the Sc/Ti/Pd/Pt electrodes in the lateral direction. The black dashed line denotes the Fermi level of ML hydrogen-passivated Bi$_2$O$_2$S$_2$ and Bi$_2$O$_2$Se$_2$, respectively. The ML hydrogen-passivated Bi$_2$O$_2$Se$_2$ data are taken from ref. 41. (b) Fermi level change from the metal to the ML MoS$_2$ device (left) and from metal to metal–ML Bi$_2$O$_2$S$_2$H and the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ device (right). The first and second changes of the Fermi level in ML hydrogen-passivated Bi$_2$O$_2$S$_2$ systems are represented by the left and right gray dashed lines, respectively. The black dashed line denotes the Fermi level of ML MoS$_2$ and ML Bi$_2$O$_2$S$_2$H$_2$, respectively. The ML MoS$_2$ data are taken from ref. 5, 15 and 62.
the Fermi level. The value of $N_0$ is $0.62 \times 10^{-2}$ and $0.80 \times 10^{-2}$ states per (eV Å$^2$) for Pd and Pt, respectively. The decay length of the MIGS $\delta$ is obtained from the linear fit of $\ln(n(E_f))$ and $z$ axis, that is $\ln(n(E_f)) = \frac{-1}{\delta} + C$. The corresponding value of $\delta$ for Pd/Pt is 3.03/2.82 Å, respectively. In addition, the electron charge $\epsilon$ is $1.6 \times 10^{-19}$ C and the vacuum dielectric constant $\varepsilon_0$ is $8.9 \times 10^{-12}$ F m$^{-1}$. Therefore, we finally get the pinning factor $S$ values for Pd/Pt electrodes as 0.23/0.19, and the average of them is 0.21, indicating a strong FLP. The strong FLP effect proves the present result.

We define the transport gap $E_g^T$ as the total of the lateral hole and electron SBH at the QTS level, namely, $E_g^T = E_g^{T,T} + \Phi_{L,T}$. The calculated values of $E_g^T$ for Ti/Sc/Pd/Pt electrodes are 1.82/1.77/2.05/2.06 eV, respectively. These values are comparable with the electronic band gap calculated for the pristine ML Bi$_2$O$_2$S$_2$H$_2$ (1.92 eV) at the DFT-GGA level.

The transfer characteristics of the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET for the Ti electrode at bias voltage $V_b = 0.64$ V are also calculated (see Fig. 10). The ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET has a high current on-off ratio up to $10^5$. SS is defined as $SS = \frac{\partial V_g}{\partial \ln(I)}$, indicating the FET gate-controlling ability. The smaller SS, the better gate controlling. We get a SS value of 270 mV dec$^{-1}$. Besides, the transfer characteristics give the largest current of 10 $326 \mu$A μm$^{-1}$.

### Discussion

In the vertical direction, both the ML Bi$_2$O$_2$S$_2$H and ML Bi$_2$O$_2$Se$_2$H band structures are destroyed for the four metals (Sc/Ti/Pd/Pt) and no vertical SBH is formed. The comparison of the energy level between ML hydrogen-passivated Bi$_2$O$_2$S$_2$ and Bi$_2$O$_2$Se$_2$ when in contact with Sc/Ti/Pd/Pt electrodes in the lateral direction is shown in Fig. 9(a). In the lateral direction, the Fermi levels of both the Sc/Ti-ML hydrogen-passivated Bi$_2$O$_2$S$_2$ and Bi$_2$O$_2$Se$_2$ systems are elevated above the CBM owing to the abnormal FLP, which results from the dipole induced by the charge redistribution at the interface, and thus a lateral n-type Ohmic contact is generated. When in contact with the Pt electrode, the Fermi level of ML hydrogen-passivated Bi$_2$O$_2$S$_2$ is pinned within the bandgap owing to the normal FLP to the MIGS, and a lateral p-type Schottky contact is formed with a hole SBH of 0.99 eV. By contrast, the abnormal FLP lifts the Pt-ML hydrogen-passivated Bi$_2$O$_2$Se$_2$ systems’ Fermi level above the CBM, and thus a lateral n-type Ohmic contact is shaped. As to the Pd electrode, it forms a lateral p-type Schottky contact with ML hydrogen-passivated Bi$_2$O$_2$S$_2$, with a hole SBH of 0.45 eV and a lateral n-type Schottky contact with ML hydrogen-passivated Bi$_2$O$_2$Se$_2$, with an electron SBH of 0.43 eV as a result of normal FLP and different MIGS positions.

The band gap of ML MoS$_2$ is 1.8 eV, which is comparable with that of ML Bi$_2$O$_2$S$_2$H$_2$ (1.92 eV). According to the theoretical and experimental results, ML MoS$_2$ prefers a lateral n-type Schottky contact when Sc, Ti, Pd, and Pt are used as the electrodes, and the calculated electron SBHs of Sc/Ti/Pd/Pt are 0.15/0.40/0.55/0.28 eV. At the lateral interface between the Sc/Ti electrode and ML MoS$_2$, the MIGS (namely a normal FLP) leads to the Fermi level slightly below the conduction band, resulting in an n-type Schottky contact. The observed pinning factor $S$ of ML MoS$_2$ is 0.097$^{63}$ and 0.105$^{64}$, indicating a strong FLP. By contrast, the abnormal FLP pins the Fermi level of ML hydrogen-passivated Bi$_2$O$_2$S$_2$ into the conduction band for Sc/Ti. Thus, Sc/Ti forms an n-type Ohmic contact with ML hydrogen-passivated Bi$_2$O$_2$S$_2$. As for Pd/Pt, the discrepancy of the contact type between ML MoS$_2$ and ML hydrogen-passivated Bi$_2$O$_2$S$_2$ can be ascribed to the different work functions. The calculated work function of ML Bi$_2$O$_2$S$_2$H$_2$ is 4.48 eV, which is apparently smaller than the value of ML MoS$_2$ (5.12 eV). Owing to the larger work function, ML MoS$_2$ tends to form an n-type Schottky contact with the Pd/Pt electrode. The comparison of the Fermi level change between the ML MoS$_2$ system and ML hydrogen-passivated Bi$_2$O$_2$S$_2$ system is shown in Fig. 9(b).

In the “SBH of the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ transistors” section, ML Bi$_2$O$_2$S$_2$H is identified to undergo metallization in the vertical direction for the Sc/Ti contact, and under such an identification, the lateral SBH obtained from the WFA method has an opposite contact property with that from the QTS method, as shown in Fig. 8. We should point out that the identification of the interfacial property is not unique. The states within the band gap of ML Bi$_2$O$_2$S$_2$H on the Sc/Ti electrode appear much less than that on the Pd/Pt electrode (see Fig. 4), and this feature also allows the tentative identification of these states for Sc/Ti-ML Bi$_2$O$_2$S$_2$H systems as MIGS. Under this identification, for Sc/Ti electrodes, ML Bi$_2$O$_2$S$_2$H forms a vertical n-type Ohmic contact because the Fermi level is above the CBM of ML Bi$_2$O$_2$S$_2$H. Thus, the contact properties of Sc/Ti in the vertical direction are fully consistent with those in the lateral direction from the QTS in terms of such an alternative identification. As for the Pd/Pt-ML Bi$_2$O$_2$S$_2$H systems, the ML Bi$_2$O$_2$S$_2$H is still identified to undergo metallization in the vertical direction, and thus the contact polarity in the lateral direction from the WFA agrees well with that from the QTS for Pd/Pt electrodes.
Conclusion

In summary, the carrier mobility of ML Bi$_2$O$_2$S$_2$H$_2$ at 300 K is calculated for the first time according to the deformation potential theory. The electron mobilities of ML Bi$_2$O$_2$S$_2$H$_2$ in the x and y directions are 26.699 and 16.447 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. ML Bi$_2$O$_2$S$_2$H$_2$ has a hole mobility of 264 and 968 cm$^2$ V$^{-1}$ s$^{-1}$ in the x and y directions, respectively. We also predict the contact characteristics of ML Bi$_2$O$_2$S$_2$H with four metals (Sc, Ti, Pd, and Pt) based on the density functional theory and first-principles quantum transport simulation. The Pd/Pt electrode shows a lateral p-type Schottky contact with ML hydrogen-passivated Bi$_2$O$_2$S$_2$ with a hole SBH of 0.54/0.99 eV. Normal FLP origins from the MIGS at the electrode-channel interface are responsible for the generation of the hole SBH. The average pinning factor S of Pd/Pt is 0.21, indicating a strong FLP. Unlike ML MoS$_2$, where a Schottky barrier is always accompanied with the bulk metal electrodes, the Sc/Ti electrode shows a desired n-type Ohmic contact with the ML Bi$_2$O$_2$S$_2$H$_2$ channel owing to the abnormal FLP, which is caused by the dipole electric field due to the charge redistribution at the interface. Finally, the transfer characteristics of the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET for the Ti electrode at $V_{GB} = 0.64$ V are calculated. The result shows that the ML hydrogen-passivated Bi$_2$O$_2$S$_2$ FET has a current on-off ratio of $10^5$ and a SS of 270 mV dec$^{-1}$. Hence, a better device performance is expected for ML Bi$_2$O$_2$S$_2$H$_2$ than ML MoS$_2$ as far as the contact resistance is concerned.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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