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Article

Unlocking the Potential of 2D WTe₂/ZrS₂ van der Waals Heterostructures for Tunnel Field-Effect Transistors: Broken-Gap Band Alignment and Electric Field Effects

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ABSTRACT: Heterostructures composed of two-dimensional materials open new avenues for advancing semiconductor technology, particularly in the development of energy-efficient tunnel field effect transistors (TFETs). Here, we employ density functional theory calculations to investigate the electronic behavior of WTe_2/ZrS_2 heterostructures having diverse dimensions and arrangement motifs. Our simulations suggest that the topmost valence band of WTe_2 overlaps with the bottommost conduction band of ZrS_{22} giving rise to the broken gap or type-III band alignment, which is favorable for fabricating TFETs. Using first-principles molecular dynamics simulations, the temperature effect on the electronic properties is studied, demonstrating that the broken gap band alignment is preserved at 300 K. Furthermore, the electronic properties of the heterostructures are shown to be affected by external electric fields: positive electric fields lead to the opposite effect. Interestingly, a Rashba-type spin splitting is observed in the topmost valence band, and the Rashba energy is slightly influenced by the



presence of external electric fields. Overall, our study sheds light on the inherent characteristics of WTe_2/ZrS_2 heterostructures and can be valuable for fabricating TFETs with optimal performance.

1. INTRODUCTION

In recent decades, technological progress has led to the creation of smaller transistors and devices incorporating billions of them on a single chip. However, as the dimensions of transistors are reduced, energy consumption and heat production become critical concerns for continued progress. In the quest to decrease energy consumption, a major challenge is achieving efficient switching between the on and off states. This is characterized by the subthreshold swing (SS) which is limited to SS > 60 mV/decat T = 300 K, known as the thermionic limit. To circumvent this fundamental limit, alternative transistor designs have been developed, like the tunnel field-effect transistors (TFETs).^{1–3} TFETs rely on quantum mechanical tunneling phenomena and exploit the band-to-band tunneling of charge carriers. When properly designed, the tunneling effect can be extremely sensitive to the gate voltage, leading to an SS < 60 mV/dec Given the need for tight electrostatic control of materials and interfaces for high-performance devices, two-dimensional (2D) van der Waals (vdW) heterostructures hold high potential for next-generation TFETs.⁴⁻⁶ Their atomically sharp interfacial regions suppress the trap-assisted tunneling, and low screening in 2D materials suggests that their band alignments are easily controlled by external electric fields (i.e., the gate voltage).

Two-dimensional transition metal dichalcogenides (TMDs) and their van der Waals heterostructures^{7–24} have been extensively examined for next-generation nanoelectronics. Two-dimensional ZrS_2 has been experimentally realized through

the electrochemical lithiation technique,²⁵ whereas large-area and uniform films have been additionally developed by atomic layer deposition.²⁶ Theoretical studies suggest that the phonon limited electron mobility of 2D ZrS₂ is 1247 cm² V⁻¹ s⁻¹ at T =300 K,²⁷ i.e., larger than the corresponding values of other wellstudied TMDs like MoS₂. Through first-principles simulations, heterostructures composed of 2D ZrS₂ have been explored and found promising for various applications such as optoelectronics,²⁸ solar energy conversion,²⁹ and photocatalytic water splitting.^{30–32} Another appealing member of the TMD family is 2D WTe₂, and nanosheets of the hexagonal phase (H-WTe₂) have been recently synthesized via a lithium-intercalationassisted technique.³³

Experimentally, the fabrication of van der Waals heterostructures, like WTe_2/ZrS_2 , is feasible through well-established methods. A common technique is mechanical exfoliation followed by deterministic stacking using a dry-transfer process, which allows for precise control over the alignment and stacking of individual monolayers. Additionally, chemical vapor deposition and atomic layer deposition are being used to grow large-

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Figure 1. Optimized models of monolayer ZrS_2 (1L- ZrS_2), bilayer ZrS_2 (2L- ZrS_2), monolayer WTe_2 (1L- WTe_2), and their most stable heterostructures (1L- $WTe_2/1L$ - ZrS_2 and 1L- $WTe_2/2L$ - ZrS_2) along with their electronic band structures. Green and orange spheres indicate W and Zr metal atoms, whereas brown and yellow spheres indicate Te and S chalcogen atoms, respectively. For the band structures of the isolated systems namely 1L- ZrS_2 , 2L- ZrS_2 , and 1L- WTe_2 the energies are referenced to the valence band maximum. For the band structures of the heterostructures, the green and orange lines indicate the contributions to the electronic states from WTe_2 and ZrS_2 , respectively. For all band structure calculations spin– orbit coupling is considered.

area monolayers and heterostructures with minimal defects. Twist angle control in such heterostructures can be achieved with manual rotation during the stacking process, providing flexibility to explore various stacking configurations.

In general, excitons, which are bound electron-hole pairs, play a significant role in the optical and electronic properties of 2D materials due to the reduced dielectric screening and enhanced Coulomb interactions in such systems. In heterostructures with a broken-gap band alignment, exciton formation at the interface can be enhanced, particularly under optical excitation. This occurs because the electron and hole can reside in different layers, leading to the formation of spatially indirect excitons. These interlayer excitons are expected to exhibit long lifetimes due to spatial separation, which can be advantageous for applications in optoelectronic devices, such as photodetectors and excitonic transistors. Additionally, the interaction of excitons with the band alignment may influence the tunneling behavior in TFETs. The energy landscape created by the broken-gap alignment could facilitate efficient exciton dissociation, with the resulting free carriers contributing to the tunneling current.

In our work, we deploy density functional theory (DFT) to explore the electronic behavior of WTe_2/ZrS_2 heterostructures, featuring various dimensions and layer distribution patterns. Our simulations show that the studied heterostructures exhibit the type-III band alignment which facilitates efficient tunneling of charge carriers. Furthermore, we find that external electric fields can affect the electronic properties of the heterostructures: positive fields increase the valence and conduction bands overlap, whereas negative fields have the opposite effect.

2. MODELS AND COMPUTATIONAL METHODS

Our first-principles calculations are carried out using the Vienna Ab initio Simulation Package (VASP),^{34,35} and for the electron-ion interaction, we use the projector augmented wave (PAW) potentials.³⁶ van der Waals heterostructures with low deformation are produced by the Cellmatch code.³⁷ We apply periodic boundary conditions, and we add a vacuum region perpendicular to the plane of the interface. van der Waals corrections are incorporated during relaxations and total energy evaluations, using the rev-vdW-DF2 functional.³⁸ For all other computations, the Perdew-Burke-Ernzerhof (PBE) functional is employed.³⁹ Our models are relaxed through the conjugate gradient method with force and energy thresholds of 0.01 eV/Å and 10^{-8} eV, respectively. An energy cutoff of 500 eV is selected for the plane-wave expansion. We employ a $16 \times 16 \times 1$ k-mesh for the relaxations of heterostructures composed of WTe₂ and ZrS_2 unit cells, whereas a 4 × 4 × 1 k-mesh is used for the relaxations of heterostructures with low deformation. Denser k-meshes are adopted for the electronic structure calculations. For computations involving external electric fields, dipole corrections are applied vertically to the interface.

Relativistic effects on the electronic properties are also explored. Based on the rev-vdW-DF2 relaxed structures, spin—orbit coupling is



Figure 2. Electronic band structures of the favorable (1×1) WTe₂/ (1×1) ZrS₂ heterostructure (considering a 4 × 4 × 1 supercell) at different temperatures. The left panel displays the band structure at 0 K. The middle panel shows the averaged band structure at 300 K, representing thermal effects on the electronic states. The right panel provides the band structures from all snapshots considered at 300 K (along with the averaged band structure at 300 K), highlighting the distribution and variance in electronic states due to thermal fluctuations. The green and orange lines indicate the contributions to the electronic states from WTe₂ and ZrS₂, respectively. For all band structure calculations spin–orbit coupling is considered.

activated, and band structure calculations are performed through the PBE functional, consistent with the approach adopted in other reports.⁴⁰ To verify the reliability of our approach, we performed additional calculations using the vdW-DF-cx functional which supports SOC.⁴¹ First, we relaxed the heterostructures using vdW-DF-cx, and then we computed the band structures using both vdW-DF-cx with SOC and PBE with SOC. Interestingly, the computed band structures are nearly identical, reinforcing the reliability of our approach. To mitigate the shortcomings in precisely predicting band gaps by DFT, the HSE06 hybrid functional is employed.⁴² To evaluate the temperature effect on the electronic properties, we carry out firstprinciples molecular dynamics (MD) considering a $4 \times 4 \times 1$ supercell and using the same parametrization scheme as the 0 K simulations. We employ the canonical NVT ensemble at 300 K and we adopt the Nose-Hoover thermostat for the temperature control.^{43,44} Our MD simulations are carried out for 10 ps using a time step of 2 fs, where the first 1 ps is considered as equilibration and we only use the last 9 ps for statistics.

3. RESULTS AND DISCUSSION

3.1. Inherent Characteristics of WTe₂/ZrS₂ Heterostructures. WTe2 and ZrS2 monolayers are composed of one hexagonal plane of metal atoms (W or Zr), sandwiched between two hexagonal planes of chalcogen atoms (Te or S). For our study, WTe_2 (ZrS_2) exhibits the trigonal prismatic (octahedral) coordination with relaxed lattice parameters of 3.533 (3.659) Å in the monolayer regime, in good agreement with previously reported simulations.^{45,46} The in-plane lattice mismatch is below 4.0%, and first, we build $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayers by placing their respective unit cells on top of each other. For our models, the total strain is shared within the layers, i.e., the WTe₂ lattice is elongated by $\sim 2\%$ whereas the ZrS₂ lattice is shortened by this amount. During the optimization process, the atomic positions are adjusted while keeping the lattice parameters unchanged. It is worth noting that test calculations where both the atomic positions and the lattice parameters are optimized are also performed, and nearly no differences are observed in the structural and electronic properties of the heterostructures. By changing the relative positions of the layers, we consider heterobilayers with six highsymmetry layer distribution patterns herein referred to as vdWH-I, vdWH-II, vdWH-III, vdWH-IV, vdWH-V, and vdWH-VI (see Supporting Information, Figure S1). We find that vdWH-IV, for which top-layer S atoms are located above Te atoms and bottom-layer S atoms lie above W atoms, corresponds to the lowest energy stack. Interestingly, vdWH-II has only 0.4

meV/atom larger energy compared to vdWH-IV. Concerning the structural characteristics, considering the most stable stack, the interlayer distance defined as the separation between the upper-layer Te atoms and the lower-layer S atoms is found to be 3.1 Å, whereas for the rest of the stacks, it spans from 3.1 to 3.7 Å (see Supporting Information, Table SI).

As a next step, we calculate the binding energies of the heterostructures through the relation

$$E_{\rm b} = E_{\rm tot}({\rm WTe}_2/{\rm ZrS}_2) - E_{\rm tot}({\rm WTe}_2) - E_{\rm tot}({\rm ZrS}_2) \qquad (1)$$

where the three terms E_{tot} (WTe₂/ZrS₂), E_{tot} (WTe₂), and E_{tot} (ZrS₂) correspond to the total energies of the heterobilayer, the isolated stretched WTe₂ monolayer, and the isolated compressed ZrS₂ monolayer. Considering the most stable stack E_b is $-23 \text{ meV}/\text{Å}^2$, and for the rest of the stacks the binding energies span from -23 to -15 meV/Å (see Supporting Information, Table SI). Note that the negative binding energies imply thermodynamically stable structures that can be experimentally synthesized.

Concerning the electronic behavior, our PBE calculations with SOC suggest that WTe2 and ZrS2 monolayers are semiconductors with band gaps of 0.79 and 1.09 eV, respectively, and our results are in good agreement with other theoretical calculations.⁴⁷ The band structure of the most stable stack is shown in Figure 1 and comparable band structures are found for the rest of the stacks (see Supporting Information, Figures S2 and S3). Interestingly, we observe that the upermost valence band (VB) originating from WTe₂, overlaps with the lowermost conduction band (CB) originating from ZrS₂, giving rise to the broken gap or type-III band alignment which is favorable for fabricating TFETs. The energy difference between the conduction and valence band edges is $\Delta E_{CBM-VBM}$ = -0.22eV. Without SOC, WTe₂ and ZrS₂ band gaps slightly increase by 0.33 and 0.03 eV, respectively, whereas for their heterostack we find $\Delta E_{CBM-VBM}$ = -0.08 eV. To mitigate the shortcomings in precisely predicting band gaps by DFT, hybrid functional calculations are additionally carried out (see Supporting Information, Figure S4). Focusing on the lowest energy heterobilayer, our HSE06 calculations without SOC revealed that the energy difference between the conduction and valence band edges is -0.12 eV. Using HSE06 with SOC the energy difference is -0.16 eV, i.e., the inclusion of SOC further increases the overlap by about 0.04 eV (see Supporting Information, Figure S5). Overall, we concluded that although the band gaps of isolated WTe₂ and ZrS₂ monolayers are



Figure 3. (a, b) Optimized model of $(\sqrt{13} \times \sqrt{13})$ WTe₂/ $(\sqrt{12} \times \sqrt{12})$ ZrS₂ heterostructure with low deformation along with its electronic band structure, (c) band alignments relative to the vacuum level prior to and after stacking, and (d) charge density difference computed by $\Delta \rho_c = \rho$ (WTe₂/ $ZrS_2 - \rho$ (WTe₂) – ρ (WTe₂) – ρ (ZrS₂). The green and orange lines indicate the contributions to the electronic states from WTe₂ and ZrS₂, respectively. Blue and yellow isosurfaces indicate electron depletion and accumulation, respectively, and an isosurface value of 0.0005 electrons/Bohr³ is selected. Spin–orbit coupling is considered in the computations.

increased in hybrid functional calculations, the broken gap band alignment of the heterostructure is preserved.

The value of the broken gap is relatively small, particularly compared to the band gap renormalization at room temperature expected for TMDs.⁴⁸ Therefore, to assess how thermal disorders affect the band alignment of WTe₂/ZrS₂ heterostructures, we carry out MD simulations at 300 K. From the MD trajectory, we extract 46 evenly spaced snapshots, and we calculate their band structure using PBE with SOC. Figure 2 shows the averaged band structure, along with the distribution of the band structures from all considered snapshots. For the sake of comparison, the band structure obtained by considering fixed atomic positions at 0 K is also shown. We observe that the band alignment is not largely affected by the temperature and the broken gap of -0.23 eV is retained at 300 K. However, the dispersion of particular electron states changes with temperature, and most notably, the uppermost valence band at Γ -point exhibits significant fluctuations with temperature, where the instantaneous energy of this band can differ by up to ~ 0.1 eV from the average value. We also examine the atomic displacements during the MD simulations by calculating the radial distribution functions (RDFs, see Supporting Information, Figure S7). We note that the temperature only results in fluctuations in the bond lengths, while the average distances between the atoms are retained (with first peaks in the RDFs agreeing well with bond lengths at 0 K, 2.74 Å for W-Te and 2.55 Å for Zr-S bonds). The widths of the first peaks in the RDF suggest fluctuations of distances between the first neighbors of about 0.2 Å for W–Te and 0.4 Å for Zr–S as compared to the 0 K values, in agreement with the smaller atomic mass of S.

For the studied heterobilayers, besides the broken-gap band alignment, a Rashba-type spin splitting is observed in the vicinity of the Γ -point, which can be particularly promising for spintronic applications (see Supporting Information, Figure S8). When ZrS₂ is placed above WTe₂ to form the heterostructure, the out-of-plane symmetry of single-layer

WTe₂ is disrupted, leading to the observation of the Rashba effect. In the K Γ direction, the maximum momentum offset and the energy difference between the band extremum and the band degenerate Γ -point are $k_{\rm R} = 0.07$ Å⁻¹ and $E_{\rm R}$ = 8 meV, respectively. It is worth noting that the Rashba splitting is rather small in these systems and considering the effect of temperature on the band structure, one can expect it to be mostly prominent at low temperatures.⁴⁹

Next, to evaluate the transport behavior, the electron effective masses are computed using the relation $1/m^* = \partial^2 E(k)/(\hbar^2 \partial k^2)$ where \hbar refers to the reduced Planck constant. For the isolated (nondeformed) single-layer WTe₂, the effective masses in the Γ K and MK directions are 0.38 and 0.42 m_o , whereas for ZrS₂ the corresponding values in the Γ M and KM directions are 1.99 and 0.30 m_o . For the most stable stack, we find $m_{e,\Gamma M} = 1.81 m_o$ and $m_{e,KM} = 0.27 m_o$ and similar results are observed in the rest of the stacks (see Supporting Information, Table SI). Overall, our findings reveal highly anisotropic electronic behavior where the light masses along the KM direction indicate high mobility contrary to the heavy masses along the Γ M direction.

Considering that the work function of WTe₂ is smaller than that of ZrS_2 ,⁴⁷ electrons instinctively migrate from WTe₂ to ZrS_2 upon stacking. Our charge analysis using the Bader formalism (performed through the PBE functional with SOC) shows that approximately 5×10^{13} e/cm² move from WTe₂ to ZrS_2 for vdWH-IV. For calculating the charge density differences, we use the relation:

$$\Delta \rho_{\rm c} = \rho(\mathrm{WTe}_2/\mathrm{ZrS}_2) - \rho(\mathrm{WTe}_2) - \rho(\mathrm{ZrS}_2)$$

where the three terms $\rho(WTe_2/ZrS_2)$, $\rho(WTe_2)$ and $\rho(ZrS_2)$ correspond to the charge density of the heterobilayer, the isolated WTe₂ monolayer and the isolated ZrS₂ monolayer, respectively (see Supporting Information, Figure S9). As anticipated, the top-layer chalcogen atoms of WTe₂ and the bottom-layer chalcogen atoms of SnS₂ primarily contribute to the charge exchange. Consistent with our charge analysis, we



Figure 4. Band structures of the favorable $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterostructure upon electric field application. The green and orange lines indicate the contributions to the electronic states from WTe₂ and ZrS₂, respectively. Spin–orbit coupling is considered in the computations.

find that WTe₂ depletes electrons whereas ZrS_2 accumulates electrons, and the heterostack looks like a miniaturized capacitor of parallel plates with an inherent electric field pointing to ZrS_2 .

In experiments, heterobilayers having different twist angles between the constituent monolayers are achievable. By varying the twist angle, we look for stacks with low deformation (less than 1%) and a minimal number of atoms (less than 100). Our considered configuration is composed of $(\sqrt{13} \times \sqrt{13})$ WTe₂ and $(\sqrt{12} \times \sqrt{12})$ ZrS₂ monolayers with a relative twist of 16°. The strain is solely distributed to ZrS₂, and various translation operations are applied. We systematically displace ZrS₂ relative to WTe₂ in the a/b directions by 0.2a and/or 0.2b, and for each displaced configuration we perform atomic optimizations. Interestingly, we find that the energy landscape is relatively flat and the energy difference between the most and least stable structures is just 0.01 meV/atom, whereas a negative binding energy of $-18 \text{ meV}/\text{Å}^2$ is computed. Concerning the electronic behavior, Figure 3 shows the band structure of the heterobilayer with low deformation and the corresponding band alignments prior to and after stacking. Note that the band alignment prior to stacking refers to the isolated nondeformed unit cells. In agreement with our previous findings, WTe2/ZrS2 heterobilayers with twisted layers exhibit the type-III band alignment. Through PBE calculations with SOC the energy difference between the conduction and valence band edges is -0.15 eV. Regarding the electron transfer, our charge analysis using the Bader formalism shows that 3×10^{13} e/cm² move from WTe₂ to ZrS₂ upon stacking.

Furthermore, we examine thicker heterostructures composed of monolayer WTe₂ and bilayer (2L), trilayer (3L), tetralayer (4L), or pentalayer (5L) ZrS₂. For few-layer ZrS₂, we consider the most stable structure where the layers are stacked on one another with no shifts or rotations.⁵¹ The relaxed lattice constants are very similar to those of single-layer, namely $a_{ZrS_2,2L} = a_{ZrS_2,3L} = a_{ZrS_2,4L} = 3.655$ Å and $a_{ZrS_2,5L} = 3.654$ Å.

Owing to the low lattice mismatch between WTe₂ and ZrS₂, we build heterostructures by placing their respective unit cells on top of each other and by sharing the strain within the layers. Initially, heterostructures composed of WTe₂ monolayers and ZrS₂ bilayers are discussed. By changing the relative positions of the layers, we consider configurations with six high symmetry layer distribution patterns herein referred to as vdWH-3L-I, vdWH-3L-II, vdWH-3L-III, vdWH-3L-IV, vdWH-3L-V, and vdWH-3L-VI (see Supporting Information, Figure S10). We find that vdWH-3L-IV, for which top-layer S atoms are located above Te atoms and bottom-layer S atoms lie above W atoms, corresponds to the lowest energy stack. Interestingly, vdWH-3L-II has only 0.3 meV/atom larger energy compared to vdWH-3L-IV, and these results are in agreement with our findings for WTe₂/ZrS₂ heterobilayers. Our PBE calculations with SOC suggest that ZrS₂ bilayer has a band gap of 1.00 eV, i.e., slightly smaller compared to the single-layer system. The band structure of the most stable heterostructure is shown in Figure 1, and similar band structures are found for the rest of the heterostructures (see Supporting Information, Figures S11 and S12). Interestingly, the broken-gap band alignment and the Rashba type spin splitting of the uppermost valence band are also observed in this system. Using PBE with SOC, the energy difference between the conduction and valence band edges is -0.23 eV, i.e., nearly the same as the corresponding value of the WTe₂/ZrS₂ heterobilayer. Next, heterostructures composed of single-layer WTe₂ and trilayer/tetralayer/pentalayer ZrS₂ are discussed. For our investigation, we consider only one configuration of high symmetry, which is structurally equivalent to the energetically favorable configurations of 1L-WTe₂/1L- ZrS_2 and 1L-WTe₂/2L-ZrS₂ heterostructures (meaning the toplayer S atoms are located above Te atoms and the bottom-layer S atoms lie above W atoms, see Supporting Information, Figure S13). Our PBE calculations with SOC suggest that the trilayers, tetralayers, and pentalayers of ZrS_2 have band gaps of 0.96, 0.95,



Figure 5. Zoomed-in view of the band structures of the favorable (1×1) WTe₂/ (1×1) ZrS₂ heterostructure upon electric field application, showing the Rashba-type spin splitting.

and 0.90 eV, respectively. Interestingly, the broken-gap band alignment and the Rashba-type spin splitting of the uppermost valence band are observed in these thicker systems (see Supporting Information, Figure S14) and the energy differences between the conduction and valence band edges are about -0.23 eV.

Lastly, we examine thicker heterostructures composed of monolayer ZrS_2 and bilayer (2L), trilayer (3L), and tetralayer (4L) WTe₂. The relaxed lattice constants of few-layer WTe₂ are very similar to those of single-layer WTe2, namely $a_{\text{WTe}_2,2\text{L}} = 3.534 \text{ Å}$ and $a_{\text{WTe}_2,3\text{L}} = a_{\text{WTe}_2,4\text{L}} = 3.535 \text{ Å}$. First, heterostructures composed of ZrS₂ monolayers and WTe₂ bilayers are addressed. By changing the relative positions of the layers, we consider configurations with six high symmetry layer distribution patterns herein referred to as vdWH-3L'-I, vdWH-3L'-II, vdWH-3L'-III, vdWH-3L'-IV, vdWH-3L'-V, and vdWH-3L'-VI (see Supporting Information, Figure S15). We find that vdWH-3L'-II, for which top-layer S atoms are located above Te atoms and bottom-layer S atoms lie above W atoms of the WTe₂ layer at the interface, corresponds to the lowest energy stack. Notably, the broken-gap band alignment is observed in these systems (see Supporting Information, Figures S16 and S17), and for the energetically favorable heterostructure, using PBE with SOC the energy difference between the conduction and valence band edges is -0.17 eV. Next, heterostructures composed of ZrS₂ monolayers and WTe₂ trilayers or tetralayers are addressed, and only one configuration of high symmetry is considered (see Supporting Information, Figure S18). This configuration is equivalent to the energetically favorable structure observed upon stacking single-layer ZrS2 and singlelayer or bilayer WTe2. Concerning the electronic properties, the thicker heterostructures exhibit the broken gap band alignment similar to their thinner counterparts (see Supporting Information, Figure S19). Overall, our simulations suggest that heterostructures of WTe_2 and ZrS_2 with diverse dimensions and arrangement motifs present the type-III band alignment which holds high potential for fabricating TFETs.

3.2. Harnessing External Electric Fields. Next, we explore the effects of external electric fields (E_{ext}) on the electronic properties of $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayers. E_{ext} is imposed vertically to the interface and positive values correspond to fields pointing to ZrS_2 . For our study, E_{ext} spans from -0.4 to 0.4 V/Å with steps of 0.1 V/Å. The electric field is considered not only in the electronic structure calculations but also in the atomic optimizations. Owing to the interface is induced, which leads to the charge carrier redistribution. The positions of the band edges are affected by the redistribution of the carriers, and Figure 4 presents the band structures of the heterobilayers in the presence of E_{ext} .

We find that for positive electric fields, WTe₂ VB edge positions move upwardly relative to the Fermi level, contrary to ZrS₂ CB edge positions. As the positive electric fields are intensified, the shifts in the band edges become more pronounced. Performing PBE calculations with SOC, by modifying the electric field from 0.2 to 0.4 V/Å the difference in energy between the VB and CB edges alters from -0.28 to -0.33 eV. Smaller energy differences correspond to larger overlaps between the valence and conduction states, implying larger electron tunneling from WTe₂ to ZrS₂. A reverse response is found for $E_{\text{ext}} < 0$, and although the overlap between the valence and conduction states decreases, the type-III band alignment is preserved. PBE calculations without SOC are also conducted and comparable results are observed (see Supporting Information, Figure S20). Furthermore, HSE calculations without SOC are carried out and the trends are similar to those of PBE (see Supporting Information, Figure S21). As



Figure 6. Band structures of $(\sqrt{13} \times \sqrt{13})$ WTe₂ $/(\sqrt{12} \times \sqrt{12})$ ZrS₂ heterostructure with low deformation upon electric field application. The green and orange lines indicate the contributions to the electronic states from WTe₂ and ZrS₂, respectively. Spin–orbit coupling is considered in the computations.

shown in Figure 5, for negative electric fields both the Rashba energy ($E_{\rm R}$) and the wavenumber difference ($k_{\rm R}$) are marginally enhanced. For instance, by modifying the electric field from 0 to -0.4 V/Å, $E_{\rm R}$ goes from 8 to 12 meV and $k_{\rm R}$ goes from 0.07 to 0.09 Å⁻¹.

As shown in Figure 6, simulations considering electric fields are also carried out for heterobilayers having twisted layers. Consistent with our earlier findings, $E_{\text{ext}} > 0$ leads to larger overlaps between the VB and CB states, contrary to our results for E_{ext} < 0. Performing PBE calculations with SOC, by modifying the electric field from 0.2 to 0.4 V/Å the energy difference between the CB and VB edges alters from -0.25 to -0.29 eV. PBE calculations without SOC are also conducted and comparable results are observed (see Supporting Information, Figure S22). Note that when SOC is neglected, a transition from the type-III to the type-II band alignment is induced for E_{ext} < 0. Also note that for $(\sqrt{13} \times \sqrt{13})$ WTe₂/ $(\sqrt{12} \times \sqrt{12})$ ZrS₂ heterobilayer, the separation between the upper-layer Te atoms and the lowerlayer S atoms is 3.4 Å, and a 0.4 V/Å electric field refers to a 1.4 V potential difference. Similarly, for $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayer the interlayer distance is 3.1 Å and $E_{\text{ext}} = 0.4 \text{ V/Å}$ refers to $\Delta V = 1.2$ V.

4. CONCLUSIONS

In this work, through first-principles density functional theory calculations, we explored the inherent characteristics of stacks consisting of WTe₂ and ZrS₂. We found that WTe₂/ZrS₂ heterostructures with diverse dimensions and arrangement motifs exhibit the type-III or broken gap band alignment which holds high potential for fabricating TFETs. Our charge analysis using the Bader formalism showed that electrons instinctively migrate from WTe₂ to ZrS₂ upon stacking and the heterostructures look like miniaturized capacitors of parallel

plates with inherent electric fields pointing to ZrS_2 . Firstprinciples molecular dynamics simulations were also performed, and we found that the type-III band alignment is preserved at 300 K. Furthermore, we examined the impact of electric fields on the electronic properties. By enhancing the positive electric fields, the overlap between the high-lying valence states of WTe₂ and the low-lying conduction states of ZrS₂ is enhanced, implying larger tunneling currents. Interestingly, besides the broken gap band alignment, a Rashba-type spin splitting was observed in WTe₂/ZrS₂ heterostructures, owing to the out-ofplane symmetry break.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.4c02738.

Optimized (1×1) WTe₂/ (1×1) ZrS₂ heterobilayers and their band structures with/without SOC; structural/ electronic properties and binding energies of $(1 \times$ 1)WTe₂/(1 \times 1)ZrS₂ heterobilayers; HSE06 band structures of (1×1) WTe₂/ (1×1) ZrS₂ heterobilayers without SOC; HSE06 band structures of the most favorable $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayer with/without SOC; snapshots of MD simulations; radial distribution functions; zoomed-in view of band structures of (1×1) WTe₂/ (1×1) ZrS₂ heterobilayers with SOC; charge density differences of $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayers; optimized stacks composed of monolayer WTe_2 and bilayer ZrS_2 and their band structures with/ without SOC; optimized stacks composed of monolayer WTe₂ and tri-, tetra-, penta-layer ZrS₂ and their band structures with/without SOC; optimized stacks composed of monolayer ZrS₂ and bilayer WTe₂ and their band structures with/without SOC; optimized stacks composed of monolayer ZrS₂ and tri-, tetra-layer WTe₂ and their band structures with/without SOC; band structures of the most favorable $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayer in the presence of external electric fields without SOC; HSE06 band structures of the most favorable $(1 \times 1)WTe_2/(1 \times 1)ZrS_2$ heterobilayer in the presence of external electric fields without SOC; and b a n d s t r u c t u r e s o f $(\sqrt{13} \times \sqrt{13})WTe_2/(\sqrt{12} \times \sqrt{12})ZrS_2$ heterobilayer in the presence of external electric fields without SOC; and b a n d s t r u c t u r e s o f $(\sqrt{13} \times \sqrt{13})WTe_2/(\sqrt{12} \times \sqrt{12})ZrS_2$ heterobilayer in the presence of external electric fields without SOC; (PDF)

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Notes

The authors declare no competing financial interest.

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