

Layer-dependent band offsets in metal/few-layer two-dimensional semiconductor junctions: Mechanisms and implications

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For electronic devices based on two-dimensional semiconductors (2DSs), few-layer transition-metal dichalcogenides offer enhanced electrical performance over their monolayer counterparts. Metal-semiconductor junctions (MSJs), which lie at the heart of such devices, incorporate not only a metal-semiconductor (M-S) interface but also multiple van der Waals semiconductor-semiconductor (S-S) interfaces when few-layer 2DSs are employed. However, the role of S-S interfaces within MSJs—particularly their interplay with the M-S interface and their potential device applications—remains poorly understood. Here, based on density-functional theory calculations, we conduct a systematic investigation of MSJs based on few-layer 2DSs (MoS_2 and InSe) contacted with both two- and three-dimensional metals. We find layer-dependent band offsets between adjacent 2DS layers, which can change sign depending on the proximity to the metal contact. This spatial variation directly results in quantized band bending that deviates from classical models. These phenomena are attributed to the interplay and competition among three effects: (1) the decay of interface dipole with distance from the M-S interface, leading to layer-resolved band bending; (2) the interlayer quasibonding mixes up the energy levels between different 2DS layers, thereby affecting the band bending; and (3) screening by partially metallized 2DS layers within the junction, which can alter the direction of band bending. Leveraging these insights, we provide an understanding of the density-functional theory calculated Schottky barrier height values for few-layer 2DSs in MSJs. Additionally, we demonstrate that the interlayer band offset can suppress direct tunneling in vertical field-effect transistors based on 2DSs.

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I. INTRODUCTION

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have emerged as one of the most promising candidates to address the scaling bottleneck of conventional transistors and construct next-generation semiconductor devices featuring ultrahigh speed, ultralow power consumption, and flexible functionalities [1,2]. In recent years, significant progress has been made for MoS_2 in large-area preparation and device fabrication [3,4]. However, fabrication-induced defects in the monolayers lead to severe Fermi-level pinning, fundamentally restricting the on-state current density. Compared with monolayer TMDs, few-layer TMDs significantly improve the carrier mobility and current-carrying capacity compared to their monolayer counterparts [5–7].

Moreover, few-layer TMDs are more conducive to realizing *p*-type contacts than their monolayer counterparts, even for MoS_2 with a large work function. This is due to the upward shift of the valence band edge in few-layer structures compared to monolayers [8–10]. Therefore, few-layer TMDs offer distinct advantages over monolayers in terms of enhanced electrical performance [8,11]. These advantages have become increasingly accessible with the recent development of layer-by-layer epitaxial growth techniques for producing high-quality few-layer MoS_2 , thereby enabling the fabrication of high-performance electronic devices based on it [12,13].

The superior properties of few-layer TMDs must be harnessed through effective electrical contacts, making the study of metal-semiconductor junctions (MSJs) paramount [14]. In few-layer systems, however, MSJs become more complex since, in addition to the conventional metal-semiconductor (M-S) interface, multiple van der Waals semiconductor-semiconductor (S-S) interfaces also emerge. At the M-S interface, an asymmetric redistribution of charge density occurs, leading to an interface dipole and a potential drop [15]. Owing to the extremely low dielectric constant in the van der Waals (vdW) gaps between 2D semiconductor layers, the potential decay proceeds in a discrete, layer-resolved manner, distinct from that in bulk or organic semiconductors (see Note

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S2 of the Supplemental Material [16] for details). Nevertheless, the role of these additional S–S interfaces—particularly their interplay with the M–S interface—remains poorly understood.

In the current work, we provide a unified understanding of the layer-resolved band bending in MSJs based on few-layer 2DSs. We show that band bending is collectively governed by multiple factors: (1) the decay of the interface dipole, which shifts the energy levels between 2DS layers; (2) the interlayer quasibonding (QB) interaction, which mixes up the energy levels in adjacent 2DS layers and has been experimentally and theoretically confirmed to be a universal phenomenon in 2D materials [10,17–19]; and (3) the screening effect within the 2DS layers—originating from metal-induced gap states or weak charge doping due to specific band alignments with the electrode—which can alter the direction of band bending. Based on the above understanding, we provide an interpretation of the density-functional theory (DFT)-calculated Schottky barrier height (SBH) value for few-layer 2DS in MSJ with top contacts, such as that obtained from layer-projected band structure. Finally, we show that the band offset between 2DS layers helps suppress direct tunneling in vertical tunneling field-effect transistors (FETs).

II. CALCULATION METHODS

DFT calculations were performed using the Vienna *Ab initio* Simulation Package [20–22]. The projector augmented-wave potentials were adopted to describe the core electrons [23]. The valence electrons were described by plane waves with a cutoff kinetic energy of 480 eV. The generalized gradient approximation for exchange-correlation potential of the Perdew-Burke-Ernzerhof form was used [24]. The vdW interactions were considered using the DFT-D3 method [25]. The Brillouin zone was sampled by $9 \times 9 \times 1$ Monkhorst-Pack k -point mesh for 1×1 unit cell and $9 \times 7 \times 1$ mesh for $1 \times \sqrt{3}$ supercell [26]. The calculation for larger systems used a similar k -point density. The convergence criteria for energy and force were set to 10^{-5} eV and $0.02 \text{ eV}/\text{\AA}$, respectively. For the simulations of MSJs, supercell structures were used. The supercell structures for the junctions are dT-MoS₂/H-MoS₂-($1 \times \sqrt{3}$), which is a rectangular cell [10], as shown in Fig. S1 of the Supplemental Material [16]; Cd₃C₂/InSe-($\sqrt{3} \times \sqrt{3}$)R30°; and Ag(111)-(2 × 2)/H-MoS₂-($\sqrt{3} \times \sqrt{3}$)R30°/T-VSe₂-($\sqrt{3} \times \sqrt{3}$)R30°. The lattice constants of the metals were changed to match that of the 2DS, since the 2DS band edges are more sensitive to strain than the metal work function [27,28]. The lattice mismatches in the junction supercells are summarized in Table SI of the Supplemental Material [16]. For the Ag(111)/H-MoS₂/T-VSe₂ junction, lattice mismatches of two heterointerfaces were accepted to balance computational feasibility and avoid the complex band structure caused by supercell-induced band folding. Besides, we verified that the band-alignment type relevant to our conclusions remains unchanged when straining the metal as shown in Fig. S2 of the Supplemental material [16]. The vacuum layer was set to be 15 Å in the z direction to avoid the spurious interaction between periodic images of the slab model [29]. To confirm that this vacuum thickness

is sufficient for the quantities discussed in this work, we performed a vacuum-thickness convergence test in Table SII of the Supplemental Material [16]. Dipole corrections were applied in all slab calculations. In addition, we checked that spin-orbit coupling of MoS₂ does not change our conclusion; refer to note S1 of the Supplemental Material [16] (see also Refs. [30,31] therein). For the bulk metal electrode modeled by a thin slab of Ag(111) in the junction, we verified that increasing the slab thickness from three to five atomic layers changes the interface dipole by ~ 0.01 eV; refer to Table SIII of the Supplemental Material [16]. More calculation details can be found in the related sections.

III. RESULTS AND DISCUSSION

Before delving into the detailed discussion of band bending types, it is imperative to first recognize the uniqueness of the few-layer 2DS with vdW gaps between them: The dielectric constant within the vdW gaps is much smaller than that within the 2DS layers themselves [32,33]. This marked difference in dielectric screening between the intralayer atomic regions and interlayer vdW gap regions [32,34] is the primary reason why band offsets between 2DS layers in an MSJ mainly occur at the vdW regions. This behavior is distinct from the continuous band bending as observed in organic semiconductors [35–37]; see Note S2 and Fig. S3 of the Supplemental Material [16]. The potential decay [in Fig. S3(b) of the Supplemental Material [16]] at vdW gaps is precisely the manifestation of interface dipole decay in vdW heterostructures. All subsequent mechanisms discussed herein are built upon this fundamental picture.

Note that, in Fig. S3(b) of the Supplemental Material [16], the depiction of band bending only considers the effect of interface dipole decay at the M–S interface, while the effects of other factors on band bending of 2DSs in MSJs remain to be elucidated, such as (1) the effect of interlayer QB interaction between 2DS layers at S–S interfaces and (2) the screening effect of the 2DS layers when they are partially metallized in a MSJ by different origins.

A. New types of band bending and mechanism

For MSJs with few-layer 2DSs, some of the possible types of band bending across 2DS layers are determined by three factors: the interface dipole at the M–S interface, the interlayer QB interaction at S–S interfaces, and the screening from partially metallized or lightly doped 2DS layers. When different factors dominate, the resulting band bending can be classified into interface dipole dominated, interlayer QB dominated, or mixed types of band bending, as shown schematically in Fig. S4 of the Supplemental Material [16]. In the case of interface dipole dominance, the decay of interface dipole away from the M–S interface leads to band offsets between 2DS layers as shown in Fig. S4(a) of the Supplemental Material [16]. Figure S4(b) of the Supplemental Material [16] corresponds to the case of QB dominance, which mixes the band edge of different 2DS layers via the formation of bonding and antibonding levels [30,38], as illustrated in Fig. 1.

Figure 1(a) shows that the QB-induced energy-level splitting between bonding and antibonding levels is $2t$, and the

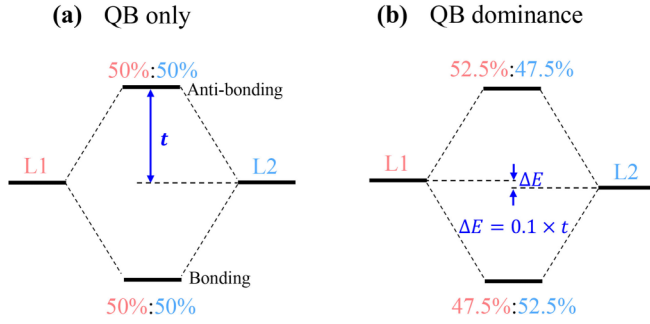


FIG. 1. The weight of layer contribution to antibonding and bonding levels for the cases of QB only and QB dominance using a simple two-level model. The interlayer-QB-interaction-induced energy splitting (corresponding to t) and interlayer energy shift (ΔE) between L1 and L2 are labeled in panels (a) and (b), respectively.

interlayer energy shift caused by the interface dipole is ΔE , as shown in Fig. 1(b). The “interlayer QB dominance” means that t is significantly larger than ΔE . Under this condition, the band-edge energy levels are an admixture of states of different 2DS layers [39].

As illustrated by the two-level model in Fig. 1(a), when the energy levels in two layers are degenerate (QB only, $\Delta E = 0$), the antibonding and bonding levels have equal contributions from the two layers. The antibonding and bonding levels are related to the valence band (VB) and conduction band (CB) edges, respectively. With a small ΔE included between the two layers in an MSJ, Fig. 1(b) shows that under QB dominance ($\Delta E = 0.1 \times t$), the layer contributions become slightly asymmetric, but the band-edge states remain mixed states of different 2DS layers. The assumption made in Fig. 1(b) that the mixing of band-edge states of different 2DS layers occurs in an MSJ (when t is much larger than ΔE) is confirmed by DFT calculations for a real system, as described in Fig. 2.

Figure 2 shows the band-edge wavefunctions and layer-projected band structure for a $\text{Cd}_3\text{C}_2/\text{InSe}(3\text{L})$ MSJ, which confirms the physical picture of “the band-edge energy levels are contributed by different 2DS layers” in the cases of interlayer QB dominance. Figure 2(a) shows that the band-edge wavefunctions of $\text{VB}@\Gamma$ and $\text{CB}@\Gamma$ are both distributed

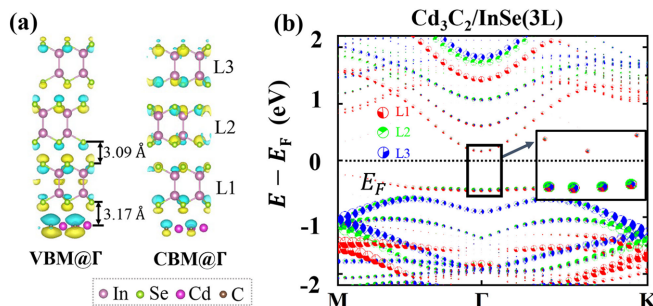


FIG. 2. Band-edge wavefunctions [panel (a)] and layer-projected band structure [panel (b)] of three-layer InSe in the $\text{Cd}_3\text{C}_2/\text{InSe}(3\text{L})$ MSJ. (a) The InSe layers are labeled as L1, L2, and L3 from bottom to top, with vertical distances of 3.17 Å for the $\text{Cd}_3\text{C}_2/\text{InSe}$ interface and 3.09 Å between the InSe layers.

in all the three layers of InSe. Figure 2(b) displays the layer-projected band structures of $\text{InSe}(3\text{L})$ in the MSJ, which also shows that VB and CB band edges are contributed by all the InSe layers. To demonstrate the interlayer QB dominance in the $\text{Cd}_3\text{C}_2/\text{InSe}(3\text{L})$ MSJ, we compare the energy-level splitting induced by the interlayer QB between InSe layers [corresponding to t in Fig. 1(a)] with the Cd_3C_2 electrode induced energy shift between InSe layers in the MSJ [corresponding to ΔE in Fig. 1(b)]. The t is estimated based on band-edge splitting from monolayer to bilayer InSe as given in Fig. S5 of the Supplemental Material [16], which shows that $2t$ exceeds 0.6 eV (or $t > 0.3$ eV) for both VB and CB. In contrast, the interface dipole in the $\text{Cd}_3\text{C}_2/\text{InSe}(3\text{L})$ MSJ is only 0.04 eV, which means that the interlayer energy shift between InSe layers (ΔE) associated with the interface dipole is smaller than 0.04 eV. In addition, we performed HSE06 calculation for the $\text{Cd}_3\text{C}_2/\text{InSe}(3\text{L})$ junction, which further confirms the conclusion from Fig. 2(b), as shown in Fig. S6 of the Supplemental Material [16]. The $\text{Cd}_3\text{C}_2/\text{InSe}$ MSJ and few-layer InSe have been studied in Refs. [40,41], which also show strong interlayer coupling between InSe layers.

In general, the QB strengths in the VB and CB can be different (e.g., for MoS_2), which may give rise to a mixed type of band bending; namely, VB and CB show different types of band bending [30,42] (see Note S3 of the Supplemental Material [16]). In Fig. S4(c) of the Supplemental Material [16], the CB bending is dominated by a combination of two factors: interface dipole and the screening effects of 2DS layer(s). In Fig. S4(c)(i) of the Supplemental Material [16], the screening effect of the first 2DS layer (due to partial metallization) may reverse the direction of CB bending from downward to upward; see Note S3 of the Supplemental Material [16] (see also Refs. [43–48] therein).

In Fig. S4(c)(ii) of the Supplemental Material [16], the band alignment between the 2D metal and the 2DS valence band leads to a weak charge transfer between them, e.g., in the MSJ formed by dT-MoS₂ and few layer H-MoS₂ [10]. The charge transfer results in weak hole doping of all the 2DS layers (with VB levels mixed by interlayer QB), and hence all the 2DS layers exhibit a weak screening effect. At each 2DS layer, the decaying interface dipole competes with the screening of the weakly doped 2DS layers: The latter can be regarded as a constant for each 2DS layer and the screening effect accumulates as the layer number (N) increases. As a result, at some 2DS layers away from the metal, the screening effect may dominate and lead to the reversion of the CB bending direction from downward to upward. To verify the above physical picture of CB bending reversion in Fig. S4(c)(ii) of the Supplemental Material [16], we present a real system in Fig. 3.

Figure 3(a) shows the layer-projected band structure of $\text{H-MoS}_2(5\text{L})$ in the dT-MoS₂/H-MoS₂(5L) MSJ. The insets show the layer-resolved conduction band edge, revealing a reversal of the CB bending direction from downward (L1–L3) to upward (L4–L5). In Fig. 3(b), the black dots represent the corresponding layer-resolved conduction band minimum (CBM) energies as given in Fig. 3(a). Then, the effective potential $V_{\text{eff}}(N)$ (black curve) is constructed from these black dots. The blue curve represents the decaying interface-dipole potential $[V(N)]$ as the solution of the one-dimensional Poisson equation.

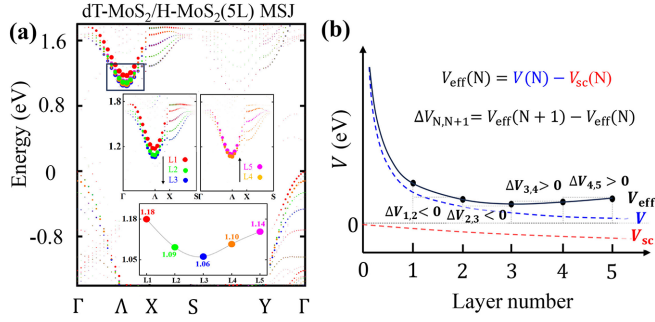


FIG. 3. Verification of the CB bending changing from downward to upward in Fig. S4(c)(ii) of the Supplemental Material [16], taking the dT-MoS₂/H-MoS₂(5L) MSJ as the example. (a) The layer-projected band structure of H-MoS₂(5L) in MSJ: The two insets in the middle show the band bending reversion from downward (L1–L3) to upward (L4–L5), and the bottom inset shows the energy values of the conduction band edge in L1–L5. (b) The effective potential in the 2DS part [$V_{\text{eff}}(N)$ with black line], which results from the competition between two effects: the decayed interface dipole [$V(N)$ with blue line] and the accumulated screening of 2DS layers [$V_{\text{sc}}(N)$, red line].

tion [35]. The red curve represents the accumulated screening of the 2DS layers with increasing layer number, and is denoted as $V_{\text{sc}}(N)$. The $V_{\text{eff}}(N)$ results from the competition between two effects: $V(N)$ and V_{sc} . Specifically, from the first 2DS layer in contact with the electrode to the N th 2DS layer away from the M-S interface, the decaying $V(N)$ competes with the accumulated $V_{\text{sc}}(N)$. Therefore, at a certain 2DS layer the accumulated screening effect can dominate over the effect of the decaying interface dipole, thereby leading to the reversal of the band bending direction from downward to upward in the

black curve of Fig. 3(b), i.e., $\Delta V_{1,2}$ and $\Delta V_{2,3} < 0$, while $\Delta V_{3,4}$ and $\Delta V_{4,5} > 0$.

The above discussions broaden our understanding of the band bending across 2DS layers for MSJs with few-layer 2DSs. These insights are valuable for advancing the studies on both top-contacted MSJs and vertical FETs. For MSJs with few-layer 2D TMDs in top contact, the presence of band offsets between the layers indicates that the conventional method for interpreting the SBH must be modified to incorporate these interlayer effects (for further discussion, see Note S4 of the Supplemental Material [16] and Refs. [48–50] cited therein). For vertical FETs, we demonstrate that the band offset between 2DS layers helps suppress the direct tunneling (Sec. III B).

B. Suppression of the direct tunneling

Two-dimensional semiconductors play an important role in achieving ultrashort channel vertical field-effect transistors [51–56], in which direct tunneling leakage is a dominant performance bottleneck. In a vertical FET based on bilayer 2DSs, the band offsets between 2DS layers offer an additional energy step that suppresses direct tunneling without increasing the channel thickness. Here, we show that the band offsets between 2DS layers help suppress direct tunneling in vertical FET (Fig. 4).

In Fig. 4, we take the Ag(111)/H-MoS₂(2L)/T-VSe₂ junction as an example. Figure 4(a) sketches the device structure. Figure 4(b) is the atomic structure adopted in DFT calculation for the analysis of band offset ($\Delta V_{1,2}$) in Figs. 4(c) and 4(d). Figure 4(c) shows the charge-density difference due to junction formation, which is calculated as $\Delta\rho(z) = \rho(\text{junction}) - [\rho(\text{Ag}) + \rho(\text{MoS}_2(2\text{L})) + \rho(\text{VSe}_2)]$, namely, the charge density of the junction minus that of the three subsystems in the junction. The $\Delta\rho(z)$ in Fig. 4(c) shows that, at the vdW

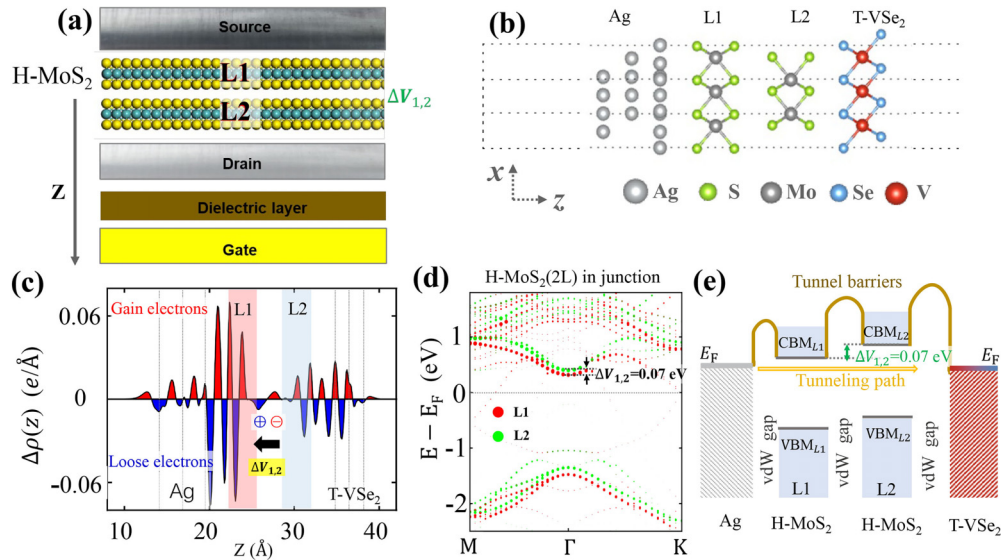


FIG. 4. A MoS₂ vertical FET with band offset ($\Delta V_{1,2}$) between MoS₂ layers using the Ag(111)/H-MoS₂(2L)/T-VSe₂ junction as an example. (a) Schematic illustration of the device structure and (b) the atomic structure in DFT calculation. (c) Plane-averaged charge-density difference due to junction formation, in which the sign change in the vdW gap between MoS₂ layers (L1 and L2) is the origin of $\Delta V_{1,2}$ (see text); and (d) the value of $\Delta V_{1,2}$ obtained from the layer-projected band structure of H-MoS₂(2L) in the junction. (e) Sketch of the tunneling with $\Delta V_{1,2}$ between MoS₂ layers.

gap between MoS₂ layers (L1 and L2), a sign change in $\Delta\rho$ appears, which leads to an interlayer dipole as sketched in this figure [57] and then results in the band offset ($\Delta V_{1,2}$) between MoS₂ layers. The origin of the interlayer dipole between MoS₂ layers in the junction with Ag and VSe₂ electrodes on the left and right can be attributed to the asymmetric coupling of the two electrodes to MoS₂. The value of $\Delta V_{1,2}$ is obtained from the layer-projected band structure of H-MoS₂(2L) in the junction, as given in Fig. 4(d). The calculated $\Delta V_{1,2}$ is 0.07 eV.

In the following, we give a simple estimation of the effect of $\Delta V_{1,2}$ on the suppression of direct tunneling. Inspired by resonant tunneling, we analyze the tunneling structure in Fig. 4(e) by employing the Breit-Wigner transmission formula [58]. The relative tunneling probability compared to resonant tunneling is approximated as

$$P_{\text{TB}} \propto \frac{\Gamma^2}{\Gamma^2 + (E_{L1} - E_{L2})^2}, \quad (1)$$

where Γ is the interlayer coupling of conduction band in bilayer H-MoS₂, and E_{L1} and E_{L2} are the energies of CBM in L1 and L2, respectively. The interlayer coupling Γ is estimated to be 0.02 eV from the averaged energy splitting of the conduction band from monolayer to bilayer, and $E_{L1} - E_{L2}$ is the abovementioned $\Delta V_{1,2}$. The estimated tunneling probability (P_{TB}) is about 8%, indicating a significant suppression of direct tunneling.

IV. CONCLUSION

In conclusion, we have identified several types of unconventional band bending that deviate from classical behavior by studying MSJs with few-layer 2DSs. We reveal the

underlying mechanisms behind these band bending behaviors, which originate from the interplay and competition among three effects: (1) the interface dipole from the M-S interface, (2) the QB interaction between 2DS layers, and (3) the screening by metallized 2DS layers within the junction. Based on these mechanisms, we provide an understanding of the DFT-calculated SBH value for few-layer 2DSs in MSJs. Moreover, we demonstrate that the interlayer band offset can suppress direct tunneling in vertical field-effect transistors based on 2DSs. These results provide a unified framework for understanding layer-resolved band engineering in few-layer 2DSs and offer a theoretical basis for the application of few-layer 2DSs in field-effect transistor devices. Experimentally, the layer-dependent band offsets may be verified by altering the number of layers and utilizing ultraviolet photoelectron spectroscopy and Kelvin probe for separate detections [59–61].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [62].

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