Epitaxial Growth and Determination of Band Alignment of Bi$_2$Te$_3$-WSe$_2$ Vertical van der Waals Heterojunctions

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**KEYWORDS:** Transition metal dichalcogenides, Topological insulators, Two-dimensional materials, Bismuth telluride, Heterojunction, Physical vapor deposition, Band alignment
ABSTRACT

Artificial heterojunctions formed by vertical stacking of dissimilar two-dimensional (2D) transition metal dichalcogenides (TMDs) monolayer materials in a chosen sequence hold tantalizing prospects for futuristic atomically thin circuits. The emergence of 2D topological insulators (TI), including Bi$_2$Te$_3$, Bi$_2$Se$_3$ and Sb$_2$Te$_3$, represents a new class of 2D building blocks and can complement the existing artificial heterojunctions as a result of their intriguing surface states protected by the time-reversal symmetry. However, the determination of band alignments of such 2D TI/TMD vertical heterojunctions, the key parameter for designing HJ-based electronic/photonic devices, which lies in the development of epitaxy growth, remains in its infancy. Here, we demonstrate the epitaxy growth of 2D TI/TMD vertical heterojunctions comprised of Bi$_2$Te$_3$/WSe$_2$ with atomically clean interfaces that are spectroscopically accessible, and theoretically tractable. Cross-sectional scanning transmission electron microscopy (STEM) images and the presence of interlayer-coupled characteristics from Raman spectroscopy collectively confirm the neat stacking of Bi$_2$Te$_3$/WSe$_2$ with the absence of unwanted containments. Microbeam X-ray photoelectron spectroscopy (µXPS) measurement coupled with the density functional theory (DFT) calculations and electrical characteristics of field effect transistors quantitatively reveals the type-II alignment of vertically stacked quintuple layers (QL) Bi$_2$Te$_3$/WSe$_2$. Meanwhile, the type-III band emerges when transitioning to multi-quintuple layers (MQL) Bi$_2$Te$_3$/WSe$_2$. The finding here provides a well-defined example of the epitaxy growth paradigm, the interlayer coupling-electronic properties relationship, for this emerging 2D TI/TMDs vertical heterojunctions.
INTRODUCTION

Semiconductor heterostructures are essential building blocks for electronic and optoelectronic devices. The emergence of vertical van der Waals (vdW) heterostructures which are made by selectively stacking of two-dimensional (2D) layered materials, including graphene, transition metal dichalcogenides (TMDs) and hexagonal boron nitride (h-BN), not only paves the foundation in realizing the atomically thin vdW layered electronics, but also transcending the fundamental limit of 3D bulk materials systems.\textsuperscript{1-2} Specifically, interfaces embedded within the atomically thin vdW heterostructures are expected to have low interfacial defects and minor inter-diffusion compared to their 3D counterparts.\textsuperscript{3} Notable examples that are at the forefront to embrace this disruptive innovation include 2D monolayer transistors,\textsuperscript{4-12} memory,\textsuperscript{13-14} highly efficient photodiodes,\textsuperscript{15-16} rectifier,\textsuperscript{17-18} and new waves of photovoltaic cells made of atomic p-n junctions.\textsuperscript{19} Among various approaches, chemical vapor deposition (CVD) and/or physical vapor deposition (PVD) hold promise to potentially reconcile the dilemma of producing high-quality 2D materials and vdW heterostructures with scalability and controlled orientation. In parallel with the efforts on metallic graphene, semiconducting TMDs and insulating h-BN, the family of vdW heterostructures has grown to include topological insulator (TI), which is on the rise and has since gained strength recently. Representative TIs include but are not limited to bismuth telluride (Bi\textsubscript{2}Te\textsubscript{3}), bismuth selenide (Bi\textsubscript{2}Se\textsubscript{3}), and antimony telluride (Sb\textsubscript{2}Te\textsubscript{3}). TI is historically well-known for their widespread uses in thermoelectric in tandem with the increasing important topological insulating properties induced by the quantum spin-Hall effect.\textsuperscript{20-22}

Bi-based TIs are characterized by the quintuple layered (QL) structure that comprises a sequential stacking of covalently bonded 2D units made of Te/Se (1)-Bi-Te/Se (2)-Bi-Te/Se (1), where (1) and (2) denote the different chemical state of anions.\textsuperscript{23} Among them, Bi\textsubscript{2}Te\textsubscript{3} has recently gained immense interest by virtue of its structural stability, earth abundance, and high carrier mobility.
Combined with the narrow bandgap (0.17 eV) and distinctive work function, Bi$_2$Te$_3$ can function as a versatile electrode for numerous electronics or optoelectronics applications. The versatility of Bi$_2$Te$_3$ can be further extended to the formation of Bi$_2$Te$_3$/WSe$_2$ vdW heterojunction (HJ) that has shown promise for the development of self-powered photodetector with a wide wavelength detection (375–1550 nm) and fast response. Despite the encouraging demonstration in device applications, determination of the workfunction ($\varphi$) of Bi$_2$Te$_3$ (4 -5.3 eV) and the associated band alignment when paired with other 2D TMDs in vdW HJ, the key parameters for designing vdW HJ-based electronic/photonic devices, remains elusive. At the root of the functional limitation is the inability to preserve the atomically abrupt, chemically intrinsic, and electrically addressable interfaces and to eliminate the mismatch in stacking orientations during the wet transfer process from CVD (PVD) grown 2D materials. Therefore, an impetus exists to explore the direct and continuous epitaxy growth in conjunction with a precise establishment of the band structures, necessary for forging ahead with a wealth suit of HJ-based electronic/photonic devices.

Here, we report the continuous epitaxy growth of 2D topological Bi$_2$Te$_3$/WSe$_2$ vertical vdW HJ with atomically clean and chemically defined interfaces that are spectroscopically accessible and distortion-free. Molecular dynamics (MD) simulation elucidates the origin of the lack of lattice distortion and mismatch, corroborating the experimental observation. Of particular importance is the ability to preserve the intrinsic and well-defined interfaces between Bi$_2$Te$_3$ and WSe$_2$, that permit us to directly measure and precisely determine the band alignment. By combining microbeam X-ray photoelectron spectroscopy (µXPS with a spot size can be focused down to ~100 nm) with density functional theory (DFT) calculations, we measure the core-level alignment across the Bi$_2$Te$_3$ and WSe$_2$ vertical vdW HJ at the nanoscale and deduce the type-II band alignment of 1QL
Bi$_2$Te$_3$/monolayer WSe$_2$. Intriguingly, we unravel the layer dependent transition in band alignment of Bi$_2$Te$_3$/WSe$_2$ HJ from type-II to type-III when the layer number of Bi$_2$Te$_3$ exceeds 1QL.

RESULTS AND DISCUSSION

**Growth of Bi$_2$Te$_3$ on Mica and WSe$_2$**

To investigate the growth of Bi$_2$Te$_3$, a commercially available mica substrate is selected as the growth template owing to its atomically smooth surface and low migration barrier energy.$^{33-34}$ Synthesis of 1QL Bi$_2$Te$_3$ was accomplished by the physical vapor deposition (PVD) process in a horizontal tube furnace. Bulk crystalized Bi$_2$Te$_3$ powders were used as the precursor and a mixture of argon (Ar) and hydrogen (H$_2$) was used as the carrier gas. In Figure 1a, images of the atomic force microscope (AFM) and optical microscope (OM) taken at the onset of growth collectively revealed the circular yet fractal morphology of 1QL Bi$_2$Te$_3$ with the lateral dimension close to 1µm. The thickness of an intrinsic 1QL Bi$_2$Te$_3$ should be around 1 nm. However, the height profiles taken along the red dotted line gives rise to an overall thickness ranging from 1.3 to 1.8 nm (more AFM images provided in Figure S1). The deviation from the standard thickness of 1QL Bi$_2$Te$_3$ can be the combined result of partially reacted amorphous precursors, strain relaxation, and adsorption layer within the vdW gap. Zhao et. al., has similarly pointed out the growth of an adsorption layer deposited consistently on top of the basal plane.$^{35}$ As the growth of Bi$_2$Te$_3$ flakes proceeded, the extremities of fractal edges of individual Bi$_2$Te$_3$ flakes impinged on one another and ultimately a polygonal 1$^{st}$ QL was formed.

In contrast to large-area continuous films of 1$^{st}$ QL Bi$_2$Te$_3$, the vertical growth of bilayer Bi$_2$Te$_3$ grown onto the top of the discontinuous 1$^{st}$ QL was observed as the PVD process extended for longer periods. Layer dependent Raman spectra are collected in Figure S2. Intriguingly, as featured in Figure 1b, the shape and dimensions of 2$^{nd}$ QL Bi$_2$Te$_3$ are juxtaposed starkly with the underlying
It can be seen that a drastic transformation in shape from a polygon to a triangle is accompanied by the substantial increase in flake dimensions between the 1\textsuperscript{st} and 2\textsuperscript{nd} QL Bi\textsubscript{2}Te\textsubscript{3}. Nucleation normally takes place on top of the 1\textsuperscript{st} QL template due to the presence of active clusters with a high diffusion barrier. Since the Bi/Te flux ratio remains constant, the growth of 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3} shall continue without external constraints while the vertical growth of 2\textsuperscript{nd} QL Bi\textsubscript{2}Te\textsubscript{3} is largely suppressed. Cross-sectional scanning transmission electron spectroscopy (STEM) in Figure 1c provides more insights into understanding the divergence in growth between 1\textsuperscript{st} and 2\textsuperscript{nd} QL Bi\textsubscript{2}Te\textsubscript{3}. In addition to the presence of individual QL of Bi\textsubscript{2}Te\textsubscript{3} separated by the vdW gaps, it can be seen that a non-crystalline interfacial layer with thickness around ~0.4 nm is epitaxially grown on top of mica substrates, corroborating the height profile determined by AFM in Figure 1a and the results from prior report.\textsuperscript{35} Supercell calculations further unveil the existence of a considerable lattice mismatch between the 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3} and mica (\(a_{\text{mica}} = 5.189\text{Å}; a_{\text{Bi}_2\text{Te}_3} = 4.385\text{Å}\), more discussion in Figure S3). In parallel, molecular dynamics (MD) simulation is used to verify the discrepancy in shape evolution, e.g., circular shape for 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3} vs. triangular shape for the successive 2\textsuperscript{nd} QL Bi\textsubscript{2}Te\textsubscript{3}. As shown in Figure 1d, the snapshots of computer-generated models represent the stages of relaxation within the 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3} on mica with an interval of 2 pico-seconds. Initially, no substantial lattice distortion was observed in the 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3}; however, the localized lattice distortion emerges as a result of the elongated bond length near the middle of the atomic planes. Note that the bonds shown in graphs have a consistent bond length of 3.25 Å. The seemingly blurring bonds can be the combined result of the elongated bond length of 3.4 Å and the underlying adsorption layer of 4 Å. Within the region below the elongated bonds, the atomic planes are clearly squeezed together. The calculation is not able to include the unknown interfacial layer, but the result of crystallographic distortion and chemical disorder qualitatively reflects the blurred atomic planes of 1\textsuperscript{st} QL Bi\textsubscript{2}Te\textsubscript{3} in
STEM (Figure 1c). Meanwhile, such distortion is substantially attenuated within the atomic planes far removed from the elongated atomic bonds, thus providing the crystalline atomic registry for the sequential epitaxy of multi-QL (MQL) Bi₂Te₃ with atomically abrupt interfaces. Together, DFT simulations, MD modeling, and STEM characterizations shed light on the strong atomic registry—vdW epitaxy correlation between the overlaying 1st QL Bi₂Te₃ and underlying mica, which in turn define the epitaxy growth strategy to form Bi₂Te₃-based vdW HJ, without the lattice mismatch constraint between the epilayer and the growth substrate.³⁶

In light of this finding, we first carry out the epitaxy growth of WSe₂ based on the previously reported approach³⁷ as a result of its high thermal stability and negligible mismatch (~0.25%) with 1st QL Bi₂Te₃. The nucleation of Bi₂Te₃ is found to prioritize on the basal plane of WSe₂ which is characterized by the lower energy barrier. The observed triangular morphology with rounded corners is attributed to the isotropic growth induced by the high amount of precursor flux.³⁸ More details are discussed in Supplementary information Figure S4. As the growth extended, distinct from the fractal edges and circular morphology of 1st QL Bi₂Te₃ on mica, patches of Bi₂Te₃ take hold in the seeding phase and then laterally merge into a complete converge on top of the WSe₂ template (Figure 2a and 2b). Height profile scanned across the red dotted line confirms the existence of 1QL Bi₂Te₃ with a characteristic thickness of 1 nm and the formation of 1QL Bi₂Te₃/monolayer (1L) WSe₂ vertical vdW HJ (Detailed AFM studied are shown in Figure S4). The Raman spectra were measured from the as-prepared MQL Bi₂Te₃/1L WSe₂ vertical vdW HJ. It is noted that direct laser irradiation is detrimental to the 1QL Bi₂Te₃ and thus interfere with the fidelity of interpreting Raman vibrational modes. Therefore, MQL Bi₂Te₃ was used instead of 1QL Bi₂Te₃ to elucidate the interlayer coupling with the underlying WSe₂ as shown in Figure 2c. The black and blue curves are denoted as pristine Bi₂Te₃ and WSe₂, respectively, and the red curve represents the vibration mode for the MQL Bi₂Te₃/1L WSe₂
vertical vdW HJ. Pronounced A$_{2g}^1$ mode at 309 cm$^{-1}$ that can be assigned to WSe$_2$ is clearly present in the MQL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. Note that A$_{2g}^1$, which is one of the out-of-plane modes, should be inactive in pristine monolayer WSe$_2$ but become visible in bilayer WSe$_2$. In addition, the A$_{2g}^1$ mode stemmed from the MQL Bi$_2$Te$_3$ was found to blue-shift to 148.3 cm$^{-1}$. It is known that A$_{2g}^1$ mode of MQL Bi$_2$Te$_3$ further shifts toward a higher wavenumber as the number of layers decreases (layer dependent Raman spectra of MQL Bi$_2$Te$_3$ are provided in Figure S2). Here, the formation of the MQL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ gives rise to an even more pronounced shift in wavenumber pertinent to the 1$^{st}$ QL Bi$_2$Te$_3$ on mica (145 cm$^{-1}$). In addition, strong interlayer coupling is also evidenced by the emergence of photoluminescence (PL) quenching in Figure S5, after epitaxy stacking with MQL Bi$_2$Te$_3$. The inception of interlayer coupling$^{31}$ between Bi$_2$Te$_3$ and WSe$_2$ is indicative of the formation of high-quality, contamination-free interfaces within the MQL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. In parallel, the selective area electron diffraction (SAED) pattern in Figure 2d, where the red and yellow hexagonal dot lines represent Bi$_2$Te$_3$ and WSe$_2$, respectively, attests to the formation of the crystallographically matched interface. The simulated diffraction patterns with corresponding lattice indexes are shown in Figure S6. The enhanced crystallinity of 1$^{st}$ Bi$_2$Te$_3$ grown on 1L WSe$_2$ is manifested in the well-defend and atomically sharp cross-section as shown in Figure 2e, where neither disordered phase at the interface nor blurred atomic contrast is discerned. Further, the energy-dispersive x-ray (EDX) spectroscopy featured in Figure S7 alluded to the absence of alloy formation at such an atomically confined interface since the growth temperature of Bi$_2$Te$_3$ is much lower than the inception temperature for chalcogen exchange (~800°C)$^{39}$ The MD simulation featured in Figure S8 also suggests the absence of lattice distortion at the 1$^{st}$ QL Bi$_2$Te$_3$/1L WSe$_2$ interface in accordance with the negligible lattice mismatch between Bi$_2$Te$_3$ and WSe$_2$ (Figure S3). Together, it becomes apparent that the combination of high thermal stability, and comparable
lattice constant of WSe$_2$ has made the epitaxy growth of (M)QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW with atomically abrupt and intrinsic interfaces possible for the comprehensive determination of band alignment.

**Band Alignment Determination of Bi$_2$Te$_3$/WSe$_2$ vertical vdW HJ**

Micro-beam X-ray photoelectron spectroscopy (µXPS) is then applied to determine the band alignment of the 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJs.$^{40}$ To prepare the samples, 1QL Bi$_2$Te$_3$/1L WSe$_2$ specimens are transferred onto an un-doped silicon substrate. Under a rapid growth condition, a wide variety of Bi$_2$Te$_3$, ranging from 1QL to MQL, can be epitaxially and simultaneously grown on the WSe$_2$ template as shown in **Figure 3a**. Exposed areas on the basal plane of WSe$_2$ flakes allows us to collect µXPS signals as the reference standard from all the constituents (**Figure 3b**). Photoelectron signals from the three designated regions are collected in **Figure 3c**, where both signatures of Bi$_2$Te$_3$ and WSe$_2$ can be clearly resolved. Since the MQL Bi$_2$Te$_3$ layers is thicker than 5 nm and have a much higher electron density, photoelectron signals and charge transfer originated from the underlying WSe$_2$ can be ruled out. Next, binding energies were measured with respect to the Fermi level (E$_F$). Here, both Bi$_2$Te$_3$ and WSe$_2$ were not intentionally doped in order to measure the intrinsic band offset characteristics of the HJs which should have their E$_F$ somewhere in the bandgaps.

We first extracted the information of the individual materials. For 1L WSe$_2$ region, the first on-set slope at 0.77 eV is the binding energy of WSe$_2$ valence-band-maximum (VBM) at gamma (Γ) point which is the second-highest valence band hill of WSe$_2$ but most sensitive to µXPS measurement.$^{40}$ W4f$_{7/2}$ is one of the characteristic peaks of WSe$_2$ that the energy difference between W4f$_{7/2}$ and VBM (Γ) can be extracted as 31.98 eV. For MQL Bi$_2$Te$_3$ region, the energy difference between its Bi4f$_{7/2}$ and VBM is elucidated to be around 157.56 eV. Note that the emergence of shoulder peak observed in MQL Bi$_2$Te$_3$ is determined to be BiO$_x$ as shown in **Figure S9**, likely the result of partial oxidation.
on the surface of MQL Bi$_2$Te$_3$. Next, the spectra collected from the region consisted of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ show both Bi4f$\frac{7}{2}$ from Bi$_2$Te$_3$ and W4f$\frac{7}{2}$ from WSe$_2$. The energy difference between these two core levels can be deduced to be $\sim$125.28 eV. Note that a red-shift of 0.35 eV is observed in W4f peak, indicating that the WSe$_2$ is p-doped by Bi$_2$Te$_3$ and the Fermi level of WSe$_2$ lies above VBM(Γ) about 0.42 eV after in contact with Bi$_2$Te$_3$. The absence of a shift in Bi4f peak can be attributed to the alignment of fermi levels driven by the charge transfer modulation between the MQL Bi$_2$Te$_3$, 1QL Bi$_2$Te$_3$ and the common WSe$_2$ template. As a consequence, Fermi levels of WSe$_2$, 1QL and MQL Bi$_2$Te$_3$ are all aligned as indicated by the yellow dashed line in Figure 3d. Thereafter, we compensate the VBM of WSe$_2$ from Γ valley up to the highest K valley by a 0.6 eV as evaluated in our earlier work. In addition, the bandgap of MQL Bi$_2$Te$_3$ is determined to be around 0.17 eV, and is found to gradually increase to 0.5 eV when the number of layers is down to 1QL.

From the simulation in Figure S10, the band edge shift comprises 69.8% from CBM and 30.2% from VBM, which can be translated into the upward shifts of 0.23 eV in CBM and the downward shift of 0.1 eV in VBM when transitioning from MQL to 1QL. Based on the μXPS result above and previously reported band gap values, the band alignment between the 1QL Bi$_2$Te$_3$ and 1L WSe$_2$ vertical vdW HJs are now established to be type-II and type-III alignments accordingly (Figure 3d).

**Density functional theory (DFT) Simulations**

To complement the μXPS results, we conduct the DFT calculations in conjunction with the projector augmented wave method as implemented in the Vienna Ab-initio Simulation Package (VASP). More details are provided in the method section. From the charge density difference map of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ in Figure 4a, we observed a significant interlayer interaction between 1L WSe$_2$ and 1QL Bi$_2$Te$_3$ alongside an intralayer charge redistribution in 1L WSe$_2$. Here, yellow and red areas represent charge accumulation and depletion, respectively.
computed band structure of 1QL Bi₂Te₃/1L WSe₂ vertical vdW HJ is shown in Figure 4b. A close-up view of the band edge region is provided in Figure 4c with Bi₂Te₃ band edges marked in red and WSe₂ band edges marked in blue, characteristic of a type-II band alignment between high symmetry K and Γ points. Further increase in the number of QL Bi₂Te₃ results in the transition of the band structure to a type-III band alignment with a significantly reduced bandgap of Bi₂Te₃ as shown in Figure 4d and 4e. On the basis of the high symmetry K and Γ points, we could further corroborate the emergence of type-III band alignment for MQL Bi₂Te₃/1L WSe₂ vertical vdW HJ. The simulated band alignments are in good agreement with our experimental μXPS result. Moreover, the valance band at Γ-point of WSe₂ elevates ~0.3 eV (bandgap decrease) in the 1QL Bi₂Te₃/1L WSe₂ vertical vdW HJ with respect to that of the pristine ML WSe₂ (Figure S11), resembling the bandgap evolution in bilayer WSe₂. In addition, an increase in the bandgap of 1QL Bi₂Te₃ to 0.332 eV in 1QL Bi₂Te₃/1L WSe₂ vertical vdW HJ contrarily deviates from the pristine value of 0.310 eV (Figure S11). These results suggest a similar trend with the aforementioned Raman spectra, where layer-dependent mode A¹g of WSe₂ emerges and A²g vibration mode of MQL Bi₂Te₃ blue shifts pertinent to that of 1QL Bi₂Te₃ on mica.

**Electrical Characteristics**

We further investigate the electrical transport characteristics of our MQL Bi₂Te₃/1L WSe₂ vertical vdW HJs as summarized in Figure 5. The vertical stacking of MQL Bi₂Te₃ on semiconducting 1L WSe₂ enables the direct fabrication of field effect transistors (FET) as demonstrated. Semiconducting channels of 1L WSe₂ and the associated source/drain contacts can be directly defined through the laser irradiation on the MQL Bi₂Te₃. Figure 5a schematically represents the design of FETs and the gating by electric double-layer. Details of laser-assisted fabrication of FETs are provided in Figure S12. It is also worth mentioning that the epitaxy and continual growth
of MQL Bi$_2$Te$_3$ on top of WSe$_2$ creates interfaces that are essentially free from Fermi pinning, crystallographic and chemical disorder$^{46}$ (Figure S13). Transfer curve (Vsd=1V) in Figure 5b indicates a typical ambipolar transport behavior of WSe$_2$, where the conduction can be switched between p-type and n-type by the gated electric field. The p-branch clearly outweighs the n-branch since the type-III band alignment facilitates the hole transport between WSe$_2$ channel and MQL Bi$_2$Te$_3$. From the established electron affinity of WSe$_2$$^{47}$ and band offset of MQL Bi$_2$Te$_3$/1L WSe$_2$ HJs determined in the above sections, MQL Bi$_2$Te$_3$ is characterized by the high electron affinity. Therefore, the MQL Bi$_2$Te$_3$ is considered to be a high φ contact to the WSe$_2$ channel. Another advantageous feature of utilizing the electronic properties from WSe$_2$ FETs is the weak Fermi level pinning effect of WSe$_2$. Electronic properties measured from the WSe$_2$ FET can be associated with the contact φ. Here, an array of WSe$_2$ FETs are fabricated with dissimilar metal contacts, e.g., different work functions, for systematically comparing the transport characteristics. To this end, palladium (Pd) that was characterized with the innate high φ ~5.3eV along with low φ titanium (Ti) (~4.3eV) are deposited, respectively, to serve as S/D electrodes. The relative energy levels for pristine 1L WSe$_2$, MQL Bi$_2$Te$_3$, Pd and Ti are schematically illustrated in Figure 5c. It has been established that the barrier height on the metal work φ is highly dependent on one of the electrical characteristics—that is, the contact resistance (R$_c$). R$_c$ for the p-branches of MQL Bi$_2$Te$_3$/1L WSe$_2$ HJs and two reference devices (Pd, and Ti based S/D electrodes) are extracted by Y-function method$^{48-50}$ (Please see supplementary materials for more details) and illustrated in Figure 5d. It becomes apparent that the R$_c$ of MQL Bi$_2$Te$_3$/1L WSe$_2$ HJs is two orders of magnitude lower than that of FETs made with a low φ Ti. On the other hand, the measured transport characteristics of MQL Bi$_2$Te$_3$/1L WSe$_2$ HJs bear a close resemblance to WSe$_2$ FETs made with a high φ contact Pd, presumably due to holes accumulating at the interfaces between Bi$_2$Te$_3$(Pd) and WSe$_2$. Nevertheless, the steep Schottky
barrier at Ti/WSe$_2$ interface impairs the hole transport as shown in the band diagram (Figure 5e). Note that the channel mobility is 47 cm$^2$/V·s for the MQL Bi$_2$Te$_3$/1L WSe$_2$ HJ transistor, suggesting that the carrier pathways at WSe$_2$ remains intact after the laser-assisted patterning. (Detailed explanation and comparison are shown in Figure S14, S15 and S16.) The investigation of $\phi$ dependent transport characteristics hence substantiates the results measured from $\mu$XPS and DFT calculations collectively.

CONCLUSION

In summary, we have developed an epitaxy growth and applied a complement of characterization approaches to elucidate the band alignment at the atomically thin and intrinsic interfaces embedded within (M)QL Bi$_2$Te$_3$/1L WSe$_2$ vdW HJ. The finding of a structural distortion during the growth of 1$^{st}$ QL Bi$_2$Te$_3$, as confirmed by cross-sectional STEM, MD simulation and Raman spectroscopy, illuminates the epaxial path toward the successful growth of (M)QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. By combining the $\mu$XPS with DFT calculations, we successfully determine the core-level alignment across the atomically thin 1QL Bi$_2$Te$_3$/WSe$_2$ vdW HJ that gives rise to the type-II band alignment with a VBO of 0.4 eV and a CBO of 1.98 eV. We further unravel the layer-dependent band alignment transition from type-II to type-III when the number of layers of Bi$_2$Te$_3$ exceeds 1QL. The FET transport behavior measured from the MQL Bi$_2$Te$_3$/WSe$_2$ HJs suggests that Bi$_2$Te$_3$ can serve as a dual role in a single device scheme: a high $\phi$ material and an efficient protection layer for the underlying semiconducting channels. From the device architecture perspective, atomically thin interfaces with a type-III band alignment enables carriers to propagate at ultra-high speeds by virtue of the unique inter-band tunneling transport property. Whereas most vdW HJs are limited to the type-I or type-II band alignment, the finding of thickness-dependent band alignment of Bi$_2$Te$_3$-WSe$_2$ HJ opens up new inroads for developing various applications such as high-speed switch
and high frequencies devices. Since the accurate determination of HJ band offset is critically important for designing vdW HJ-based electronic/photonic devices, the work demonstrated here paves the basis for integrating Bi₂Te₃-based vdW HJ as a critical component for electronics and optoelectronics.

METHODS

**Growth of Bismuth telluride (Bi₂Te₃).** Mica (Muscovite, V3 grade, from Electron Microscopy Sciences) is freshly cleaved before placing at the downstream of a horizontal furnace. Bi₂Te₃ powder is placed at the center of furnace serving as a precursor. CVD system is firstly pumped down to the base pressure of 0.1 mTorr, followed by introducing 65 sccm Ar and 5 sccm H₂ as carrier gases. The furnace temperature is ramped up to 350°C and kept for 5-15 min to initiate the growth of Bi₂Te₃. The growth temperature on the substrate at the downstream side is measured to be 250°C. The same procedure is adopted for the growth of 1QL Bi₂Te₃ on WSe₂ epilayer where the mica substrate is replaced by the as-grown WSe₂ flakes on sapphire.

**Raman, Photoluminescence (PL) Spectroscopies and Scanning Transmission Electron Microscopy (STEM).** Optical spectroscopy is taken under a Witec alpha 300R confocal Raman microscopic system. Gratings of 1800 meshes/mm and 300 meshes/mm are selected for high resolution Raman spectrum and wide range PL spectrum respectively. The TMDs are excited by a 532 nm laser with a power of 1 mW and a spot size of 0.5 μm. Raman signal is collected by a 100X objective (N.A = 0.9) from a Carl Zeiss Microscopy. Cross-sectional STEM imaging and EELS mapping data were conducted using JEOL JEM-ARM200F and GATAN Quantum 965 EELS camera operating at 200 kV.

**Density Functional Theory (DFT).** For VASP calculations, the generalized gradient approximation in the Perdew-Burke-Ernzerhof parametrization is employed for the exchange-correlation potential.
The plane wave cutoff energy is set to a sufficiently large value of 500 eV. The van der Waals interaction between constituent systems is taken into account using the non-local optB86b-vdW density functional as successfully employed before for the Bi$_2$Te$_3$ quintuple layer. To get accurate band offsets for few QL Bi$_2$Te$_3$, we used SCAN+rVV10 density functional. In order to avoid lattice mismatch between constituent systems, we build $\sqrt{7} \times \sqrt{7} \times 1$ supercell of Bi$_2$Te$_3$ matched to mica at a rotation angle of 19.1°. Similarly, we use a $\sqrt{7} \times \sqrt{7} \times 1$ and 2×2×1 supercells of monolayer WSe$_2$ and Bi$_2$Te$_3$, respectively, giving rise to a lattice mismatch of less than 1%. Due to the large number of atoms involved in Bi$_2$Te$_3$/mica HJs, only gamma-point is used to achieve convergence, whereas for Bi$_2$Te$_3$/WSe$_2$ HJs, a gamma-centered Monkhorst-Pack 6×6×1 k-mesh is used for the structural relaxation. In the self-consistent calculations, the Brillouin zone integration is performed by a denser 12×12×1 k-mesh. For the iterative solution of the Kohn-Sham equation, we ensure an energy convergence of $10^{-6}$ eV and force convergence of $10^{-3}$ eV/Å in the structural relaxation. The effects of spin-orbit coupling are taken into account in the band-structure calculations.

We use a 15 Å thick layer of vacuum on top of the HJs to exclude spurious interaction between periodic images in the out-of-plane direction as three-dimensional periodic boundary conditions are applied. We plot the results using Matplotlib software package.

**Device Fabrication.** MQL Bi$_2$Te$_3$ is firstly grown on top of monolayer WSe$_2$. Source/drain (S/D) electrodes comprised of Pd (10nm)/Au (50nm) are thermally deposited via an e-beam evaporator, followed by a lift-off and a remote ion etching (RIE) process to identify the effective regions of measurements. The WSe$_2$ channel region is defined by a laser-scanning assisted removal on Bi$_2$Te$_3$. The laser scanning is conducted under a Witec alpha 300R confocal Raman system with an output power of 1 mW and a spot size of 0.5 µm. Ionic liquid, (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide), is used as the top gate to electrostatically modulate the
conductivity of the channel. Schematic representation and detailed production schemes are shown in Figure S12.

ACKNOWLEDGEMENTS

V.T., and M.-H.C. are indebted to the support from the King Abdullah University of Science and Technology (KAUST), KAUST Catalysis and Solar Centres, and Office of Sponsored Research (OSR) under Award No: OSR-2018-CARF/CCF-3079. S.S. thanks High Performance Computing Center North (HPC2N) National Supercomputer Center in Linkping (NSC) for allocation of time and resources, through the Swedish National Infrastructure for Computing (SNIC). H.-L.T. acknowledges the partial support from the Ministry of Science and Technology of Taiwan (MOST-108-2917-I-564-036). We thank Prof. D. A. Muller and Dr. Z. Chen for the helpful discussion on STEM and Prof. Q. Tong for the useful discussion on DFT simulations.

Supporting Information Available: Figures S1-S16 are included. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES


Figure 1. Growth of Bi$_2$Te$_3$ on mica. (a) AFM image of 1QL Bi$_2$Te$_3$ flakes. Inset shows the corresponding optical microscopic image. The height profile taken along the red dashed line gives rise to the step height of ~1.8 nm. (b) AFM image of triangular MQL Bi$_2$Te$_3$ flakes with a height profile measured along the red dashed line. (c) Cross-sectional STEM of MQL Bi$_2$Te$_3$/mica. The blurring area in red indicates the distorted region. (d) Snapshots (side view) of 1QL Bi$_2$Te$_3$/mica before (left) and after (right) ab-initio molecular dynamics simulations at 350 K after 2 ps.
Figure 2. Epitaxial growth of 1QL Bi$_2$Te$_3$ on 1L WSe$_2$. (a) Optical image of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical heterojunctions. Red and blue dashed lines represent Bi$_2$Te$_3$ and WSe$_2$, respectively. (b) AFM image of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ with a height profile taken along the red dashed line across the HJ. (c) Raman spectra of MQL Bi$_2$Te$_3$ (line in black), Bi$_2$Te$_3$/WSe$_2$ vertical vdW HJ (line in red) and WSe$_2$ (line in blue). (d) SAED pattern of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ, where red and light blue hexagonal dot lines represent Bi$_2$Te$_3$ and WSe$_2$, respectively. (e) Cross-sectional STEM of MQL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ.
Figure 3. Determination of band alignment of (M)QL Bi\textsubscript{2}Te\textsubscript{3}/1L WSe\textsubscript{2} vertical vdW HJ. (a) Optical image of (M)QL Bi\textsubscript{2}Te\textsubscript{3}/1L WSe\textsubscript{2} vertical vdW HJ with three marked points of WSe\textsubscript{2}, vertical vdW HJ, and MQL Bi\textsubscript{2}Te\textsubscript{3}. (b) Schematic representation of the three marked points in (a) for µXPS measurement. (c) µXPS spectra of WSe\textsubscript{2}, MQL Bi\textsubscript{2}Te\textsubscript{3} and vertical vdW HJ with their VBM (color in black), W4f (color in green), and Bi4f (color in purple) peaks. (d) Established band alignment from µXPS spectra in (c) of 1L WSe\textsubscript{2} with 1QL and MQL Bi\textsubscript{2}Te\textsubscript{3}. 
Figure 4. DFT simulation of Bi$_2$Te$_3$/WSe$_2$ vertical vdW HJ. (a) Charge density difference map of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. Yellow and red regions represent charge accumulation and depletion, respectively. (b) Band structure of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. (c) A close-up view of band structure of 1QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ, which shows a type II band alignment. Red and blue dashed lines represent the band edges of Bi$_2$Te$_3$ and WSe$_2$, respectively. (d) Band structure of 2QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ. (e) Zoomed-in band structure of 2QL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ, which shows a type III band alignment.
Figure 5. Electrical characterizations of MQL Bi$_2$Te$_3$/1L WSe$_2$ vertical vdW HJ-based field effect transistors. (a) Schematic illustration of a representative MQL Bi$_2$Te$_3$/1L WSe$_2$ based transistor, where monolayer WSe$_2$ serves as the semiconducting channel and MQL Bi$_2$Te$_3$ acts as the source/drain contacts. Device is gated by an ionic liquid. (b) Transfer curves with V$_{ds}$ = 1 V. (c) Estimated band alignment with different work function metals before forming the contact. (d) Comparison of contact resistance under three difference device schemes. (e) Schematic representation of band alignment of WSe$_2$ with three different S/D contacts.
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