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Selective Hydrogen Etching Leads to 2D Bi(111) Bilayers on Bi₂Se₃: Large Rashba Splitting in Topological Insulator Heterostructure

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Supporting Information

ABSTRACT: Ultrathin bilayers (BLs) of bismuth have been predicated to be a two-dimensional (2D) topological insulator. Here we report on a new route to manufacture the high-quality Bi bilayers from a 3D topological insulator, a top-down approach to prepare large-area and well-ordered Bi(111) BL with deliberate hydrogen etching on epitaxial Bi₂Se₃ films. With scanning tunneling microscopy (STM) and X-ray photoelectron spectra (XPS) in situ, we confirm that the removal of Se from the top of a quintuple layer (QL) is the key factor, leading to a uniform formation of Bi(111) BL in the van der Waals gap between the first and second QL of Bi₂Se₃. The



angle resolved photoemission spectroscopy (ARPES) in situ and complementary density functional theory (DFT) calculations show a giant Rashba splitting with a coupling constant of 4.5 eV Å in the Bi(111) BL on Bi₂Se₃. Moreover, the thickness of Bi BLs can be tuned by the amount of hydrogen exposure. Our ARPES and DFT study indicated that the Bi hole-like bands increase with increasing the Bi BL thickness. The selective hydrogen etching is a promising route to produce a uniform ultrathin 2D topological insulator (TI) that is useful for fundamental investigations and applications in spintronics and valleytronics.

■ INTRODUCTION

Topological phases in condensed matter systems have attracted intense worldwide research interest in the past decade.¹⁻⁵ Among these novel phases, quantum spin Hall (QSH) insulators or so-called two-dimensional (2D) topological insulators (TIs), which host exotic surface electronic structure, are promising to apply to building next-generation low-power spintronic devices.^{5–8} Three-dimensional (3D) TIs feature a bulk energy gap and time-reversal symmetry-protected gapless surface states originating from spin-orbit coupling (SOC), which is distinct from the conventional band insulator. The Dirac fermions on the surface of a TI possess a definite

chirality, which is associated with the one-to-one electron spin and momentum locking, resulting in a nontrivial quantum Berry phase that suppresses the backscattering and localization of carriers. Although many materials have been demonstrated to be 3D TIs, a QSH insulator is still very rare. The HgTebased quantum well (QW) was first proved to be a QSH insulator experimentally,^{9,10} but these HgTe QWs have serious limitations, such as toxicity, difficulty of processing, and

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incompatibility with present silicon-based electronic technology. It is also difficult to have precise control of these materials to perform such delicate experiments. Alternatively, research on 2D TIs with a large gap became intensive. For example, many efforts have been made to probe candidate compounds of large gap 2D TIs, such as Ge,^{11,17} Sn,^{12,13} Sb,¹⁴ and Bi.¹⁵⁻¹⁷ Among them, Bi has the strongest SOC strength that results in novel spin-split surface states.^{18–25} Moreover, the Bi(111) surface forms a bilayer-terminated structure, with a buckled honeycomb lattice that leads to valleys in the surface-band structure, $^{24-26}$ which is similar to many other 2D valley materials with a honeycomb lattice. $^{5,27-29}$ A few bilayers of Bi(111) are predicted to have a 2D TI-supporting QSH effect, leading to the interesting one-dimensional (1D) topological edge state.^{30,31} Several studies have aimed to prepare a Bi bilayer by using different methods such as molecular beam epitaxy,³²⁻⁴³ exfoliation,⁴⁴ or investigation of step edges of a Bi(111) surface.45

Recently, it was reported that Bi_2Se_3 samples cleaved in ultrahigh vacuum (UHV) spontaneously form a Bi bilayer on the topmost QL at room temperature.⁴⁶ Furthermore, Bi accumulation may occur at the Bi_2Se_3 surface via diffusion of Bi⁴⁷ that can be intercalated between the QLs.^{48,49} In contrast, Hewitt et al.⁵⁰ reported that Bi_2Se_3 crystals cleaved in UHV predominantly show Se surface termination, while those stored in air for a long time have a high probability of Bi termination.

Despite these previous investigations, it remains unclear how the morphology and electronic properties of the Bi_2Se_3 surface are modified upon and controlled by exposure to hydrogen atoms, which could be very invasive for the surface.⁵¹ Moreover, there is a lack of studies of thickness-dependent band structures of Bi bilayers. Most importantly, the bottom-up approach to prepare Bi BLs is complicated, which greatly limits the film's quality with two distinct phases (Bi(111) and Bi(110))⁴³ and decreased grain size. The band structures of Bi/ TIs had been theoretical predicted;^{48,52} however, these results are inconsistent with other experiments. The physics of the interface between a topological insulator and a Bi has largely been left unexplored.

In this paper, we report the preparation of Bi(111) bilayers with a uniform and flat surface via a top-down method using deliberate atomic-hydrogen etching. With STM and XPS in situ, the atomic view and the mechanism according to which hydrogen reacts with Bi₂Se₃ are revealed for the first time. The results show that the removal of Se elements begins from the top and bottom of a quintuple layer (QL), leading to the formation of Bi(111) bilayers in the van der Waals (vdW) gap. ARPES record in situ and complementary DFT calculations show that a large Rashba splitting exists, which is attributed to the large SOC and potential gradient at the interface between Bi(111) BL and Bi₂Se₃. Strong hybridization between BL and the TI interface QL causes the topological surface states of Bi₂Se₃ to move to deeper QL to maintain a nontrivial band topology of the entire system. The band structures of the Bi(111) bilayers, dependent on thickness, have been traced with ARPES. By tuning the exposure to atomic-hydrogen etching, we can directly control the thickness and band structures of the Bi bilayers. Our approaches and results not only enlighten the nature of 2D TI from 3D TI but also pave a new way to design Bi-based topological materials and devices for applications.

EXPERIMENTAL SECTION

Sample Preparation. To grow Bi₂Se₃ films on an Al₂O₃(0001) substrate, a c-plane sapphire substrate was cleaned with a standard procedure before being loaded into a growth chamber. To remove possible contaminants from the substrate surface, the sapphire substrate was heated to 1000 °C for 1 h. Highly pure Bi (99.99%) and Se (99.999%) were evaporated from a Knudsen cell; the fluxes were calibrated in situ with a quartz-crystal microbalance. The base pressure of the molecular beam epitaxy (MBE) system (AdNaNo Corp., model MBE-9) was less than 2×10^{-10} Torr; the growth pressure of the Bi₂Se₂ thin film was maintained below 1×10^{-9} Torr. The growth rates were controlled at a typical value 0.2-0.3 QL/min. The substrate was maintained at 290 °C during the growth; this temperature was chosen on the basis of our earlier experimental data on Bi₂Se₃ thin films, which revealed that this growth temperature optimized the film quality.53 The Bi and Se material fluxes were generated with effusion cells and calibrated in situ using a quartz-crystal microbalance. Reflection high-energy electron diffraction (RHEED) in situ was used to monitor the quality of the film. A streaky RHEED pattern was observed, indicating that the substrate was a single crystalline epi-ready substrate and could be used for the MBE growth of the Bi₂Se₃ film. Se (thickness 10 Å) was deposited on the Bi₂Se₃ film after the films were cooled to 23 °C. The samples were transferred into the load-lock of the measurement systems via ambient environment after being taken from the dedicated MBE system.

STM Characterization. The STM experiments were performed in an ultra-high-vacuum (UHV) system (JSPM-4500 A/S; JEOL Ltd.) with base pressure 1.5×10^{-10} Torr. The system consisted of a samplepreparation chamber and a variable-temperature STM/AFM observation chamber equipped with a cooling tank.⁵⁴⁻⁵⁶ The samples were introduced into a preparation chamber with base pressure 3.7×10^{-10} Torr in which decapping was performed. In the direct desorption, the samples were heated from 23 to ~180 °C, at which point the Se capping layers were removed. The entire decapping required about 1 h. Deliberate hydrogen exposures were performed on the Bi2Se3 surface at 23 °C using an atomic-hydrogen source. A flux of atomic hydrogen (H) was produced from hydrogen molecules (H₂) that were cracked on a hot tungsten filament (about 1800 °C, approximately 25 cm from the sample). For the quantification of the exposure of the sample, we use Langmuir (L) units (1 L = 1.0×10^{-6} Torr s) in the following. Immediately after hydrogen etching, the sample was transferred into the STM measurement chamber under UHV conditions. All the STM measurements were conducted at 23 °C; data were collected in a constant current mode. High-resolution topographic STM images were then captured with electrochemically etched tungsten wires. Before the Bi₂Se₃ surface was imaged, the tip was placed a few micrometers away from a silicon substrate that had been heated to 1200 °C, indirectly heating and cleaning the tip. The tip was also cleaned on applying voltage pulses during the STM operation. As the STM tip is known to influence the size and structure of the atoms, to minimize any artifact from the tip and the STM electronics, the images presented in this work were selected only following repeated scans of the same surface region and the evaluation of various similarly obtained images.

XPS and ARPES Characterization. The XPS and ARPES experiments were performed at beamlines 24A and 21B1 of the Taiwan Light Source in the National Synchrotron Radiation Research Center (NSRRC). The MBE-grown Bi_2Se_3 covered with a Se capping layer was annealed at 180 °C for about 1 h in an UHV environment to remove the capping layer before XPS and ARPES measurements. After that, Bi bilayers were formed on a Bi_2Se_3 thin film with atomic-hydrogen etching *in situ* in the preparation chamber. The XPS data of Bi 5d were recorded with an SPEC Phoiboss150 energy analyzer with photon energy 200 eV. The incident photon energy was calibrated on recording the Au 4f core levels. The ARPES data were measured in a UHV chamber equipped with a hemispherical analyzer (Scienta R4000) with collecting angle $\pm 15^{\circ}$ at the BL21B1 beamline in NSRRC. All spectra were recorded at 80 K and base pressure 5 × 10⁻¹¹ Torr with incident photon energy 20 and 58 eV. The angle

resolution was about 0.2° , and overall energy resolution was better than 12 meV. The Dirac point of the surface state was determined by an analysis of the momentum distribution curves (MDCs).

Computation. The DFT calculations for Bi(111) n-BLs on the Bi₂Se₃ 6QL slab model were performed on the basis of the generalized gradient approximation (GGA)⁵⁷ using the projector augmented-wave method⁵⁸ as implemented in the Vienna *ab initio* simulation package (VASP).⁵⁹ The experimental lattice parameter (4.1 Å) was used for the Bi₂Se₃ subtract; the lattice parameter of Bi(111) n-BL was constrained to match the substrate. We fixed the Bi₂Se₃ in the bottom 4 QL and relaxed the top 2 QL and the Bi(111) n-BL until the residual forces were less than 0.01 eV/Å. The SOC was included self-consistently in the calculations of electronic structures with a Monkhorst–Pack *k*-point mesh 15 × 15 × 1; the vacuum thickness was larger than 20 Å to ensure the separating of the slabs.

RESULTS AND DISCUSSION

Figure 1a presents a large-scale image of the Bi_2Se_3 film (thickness 80 nm); both the large, atomically flat terraces and



Figure 1. (a) Topographic STM image of Bi_2Se_3 film (300 × 300 nm², $V_s = 2$ V, I = 0.15 nA). (b) Line scan profile corresponding to the black line in part a. (c) Atomically resolved STM image (5 × 5 nm², $V_s = 3$ mV, I = 0.15 nA). (d) Band dispersion image along the Γ -K direction for a bare Bi_2Se_3 film (hv = 58 eV). The inset shows the LEED pattern corresponding to part a.

the straight steps are indicators of the high-quality film. The sharp low-energy electron diffraction (LEED) pattern also reflects the satisfactory crystalline quality of the film, as shown in the inset of Figure 1a. The triangular shape of the islands is consistent with the lattice symmetry of the Bi₂Se₃(0001) surface. The measured line profile of the height in Figure 1b (line scan in Figure 1a) shows that the steps have height 9.5 Å, corresponding to a quintuple layer of the Bi2Se3 structure.^{60,61} The atomically resolved STM image (Figure 1c) reveals the hexagonal lattice structure of the Se-terminated surface of the Bi₂Se₃ film.^{62–64} Figure 1d shows the result of band mapping of the Bi_2Se_3 thin film. Two bands with nearly linear dispersion at the Γ point, forming a Dirac cone, correspond to the characteristic gapless surface state of Bi2Se3. The Dirac point is located at binding energy -0.4 eV. These results indicate that the present MBE-grown Bi₂Se₃ sample is highly crystalline and behaves as an n-type semiconductor.

Soon after the MBE-Bi₂Se₃ thin film was transferred *in situ* to an STM chamber, the surface of Bi₂Se₃ was exposed to a

hydrogen atom environment at room temperature (RT), and the evolution of the morphology of the Bi₂Se₃ film with increasing doses of hydrogen atoms was studied with STM images in a sequence, as shown in Figure 2. The amount of hydrogen atoms exposed on the Bi₂Se₃ surface up to 50 L had an evident change of the straight step edge into a serrated (wavy) step-edge appearance, as shown in Figure 2a. For hydrogen at dosage 90 L some nanoscale voids appear on the terraces, indicating that Se atoms were removed from the terrace sites, as shown in Figure 2b. With increasing hydrogen atom dosage to ~180 L, large fractional Se layers were etched, resulting in residual Se islands on the Bi-terminated terraces as seen in Figure 2c. Figure 2d displays a striking change in the surface morphology upon hydrogen dosing to 360 L; dispersed and isolated Se islands as well as large and flat terraces with triangular and hexagonal-like opening were observed. The edge orientation of the triangular and hexagonal-like opening is consistent with crystallographic orientation of the underlying Bi₂Se₃. Additionally, small amounts of islands with selfpatterned structure emerged, as indicated by black arrows in the inset of Figure 2d, the appearance of Bi BL. Nevertheless, the atomic structure and patterns inside the opening are vaguely visible. With increasing dosage of hydrogen atoms to 720 L, the STM images became remarkably enlarged, as shown in Figure 2e. A significantly opening area with a clear selfpattern structure was clearly observed, while hydrogen atoms to 1080 L led to the formation of self-patterned terrace with large area (>100 nm \times 100 nm) for the entire surface in Figure 2f. The periodicity of the self-pattern is displayed as black dots in Figure 2g. The self-patterned morphology is a characteristic of the Bi bilayer formation on Bi_2Se_3 .^{42,43} According to the line scan in Figure 2g, the measured step height 0.4 nm and the buckling corrugation height 0.1 nm in the line profile are consistent with the periodically buckled structure of Bi BL, which is formed to release the strain caused by the lattice mismatch between Bi BL and Bi₂Se₃(0001).^{42,43} The zoom-in image of the periodically buckled structure in Figure 2h,d displays an ordered hexagonal periodic array of bright protrusions of the Bi atoms. The line profile in Figure 2j (line scan in insert of Figure 2h) indicates that the lattice spacing of the Bi(111) is 0.44 nm, which is about 8% larger than that of $Bi_2Se_3(0001)$, ~0.41 nm. As a result, the selfpatterned structure resembles a moiré pattern,⁴² which originates from the in-plane lattice constant mismatch between Bi(111) and Bi_2Se_3 . The interlayer distance and the lattice parameter of the bulk Bi(111) surface are 0.394 and 0.454 nm, respectively.²⁶ The lattice parameters determined with the STM are near those of bulk Bi(111). With the hydrogen-etching method, the Bi film is formed with stacking of a Bi bilayer consisting of two hexagonal lattices along direction [111]; as a result of stress release, the Bi(111) surface adopts a highly buckled honeycomb structure. The protrusions in the STM image reflect the arrangement of the upper atoms in the buckled honeycomb structure. These results indicate that the geometric structure of the Bi(111) BL formation on Bi_2Se_3 is similar to that of the (111) surface of a Bi single crystal.²⁶

The evolution of the surface chemistry due to hydrogen etching was probed with measurement of X-ray photoemission spectra (XPS). Figure 3a displays the changes in XPS spectra of Se 3d at 360 and 1080 L. The Se 3d core level contains only a single doublet, representing the Se $3d_{5/2}$ and Se $3d_{3/2}$ orbitals, with peak positions 53.44 and 54.29 eV, respectively.^{47,61,65} The attenuation of intensities of the Se 3d peaks was proportional to

Figure 2. STM images obtained after dosing with hydrogen at (a) 50 L (300 × 300 nm², $V_s = 0.1$ V, I = 0.15 nA), (b) 90 L (200 × 200 nm², $V_s = 0.1$ V, I = 0.20 nA), (c) 180 L (90 × 90 nm², $V_s = 0.1$ V, I = 0.1 nA), (d) 360 L (200 × 200 nm², $V_s = 1$ V, I = 0.1 nA), (e) 720 L (300 × 300 nm², $V_s = 1$ V, I = 0.15 nA), (f) 1080 L (300 × 300 nm², $V_s = 1.0$ V, I = 0.1 nA). (g) The periodicity of the self-pattern of Bi BL (100 × 100 nm², $V_s = 1.0$ V, I = 0.18 nA). (h) Zoom-in STM image of the periodically buckled structure (10 × 10 nm², $V_s = 4$ mV, I = 0.2 nA). Inset is atomically resolved STM image of Bi BL. (i, j) Line scan profile corresponding to the black line in part g and the blue line in the inset of part h, respectively. The insets show the magnified STM images (inset images of (d) 100 × 100 nm², (e) 62 × 62 nm², and (h) 5 × 5 nm²).

Figure 3. XPS of (a) Se 3d peaks and (b) Bi 5d peaks before and after dosing hydrogen at 360 and 1080 L, respectively.

the amount of hydrogen dosage, as the depletion of Se occurs on the surface of Bi_2Se_3 film. Figure 3b displays the evolution of the Bi 5d XPS core-level spectra as a function of the H dose. Before exposure to hydrogen atoms, the Bi 5d XPS of the Bi_2Se_3 film contains the characteristic doublet representing the Bi $5d_{5/2}$ and Bi $5d_{3/2}$ orbitals with peak position 24.94 and 27.99 eV, respectively. These peaks are labeled as Bi–Se, because of a characteristic of bismuth bonded to selenium within the Bi₂Se₃ quintuple layer unit. These positions are consistent with preceding measurements on these Bi₂Se₃ films and single crystals.^{47,61,66} At 360 L, an additional component that appeared at the side of smaller binding energy in the region of the Bi–Se doublet can be labeled as a bonding characteristic of Bi–Bi at 23.91 and 26.98 eV, respectively.^{47,66} The Bi–Se component and peak position are greatly attenuated and shift ~0.08 eV to smaller binding energy, as a change occurred in the surface of Bi₂Se₃ after H etching. At 1080 L, the Bi–Bi feature dominates the XPS; a small shoulder indicates that metallic bismuth existed on the surface of the Bi₂Se₃ thin film. The XPS results agree satisfactorily with the STM result.

According to the STM and XPS results, the formation of Bi BL via H etching is schematically illustrated in Figure 4. The rhombohedral crystal structure of Bi_2Se_3 consists of five atomic layers, known as quintuple layers (QL), arranged along direction (0001), in the order Se(I)-Bi(I)-Se(II)-Bi(I')-Se(I'), as shown in Figure 4a. The interaction between the neighboring QL is of a vdW type, as a plane of the crystal along direction (0001) between two QLs with Se termination.^{3,61} Atomic hydrogen can react with Se atoms in Bi_2Se_3 and become hydrogen selenide gas.^{67,68} For a small amount of hydrogen atoms, the Se atoms located in the outermost surface region, i.e., mainly Se atoms at Se(I) site and a few in the step edge, are

Figure 4. Schematic diagram of the mechanism of hydrogen etching; blue and red spheres correspond to bismuth and selenium atoms, respectively.

Figure 5. High-resolution ARPES result along direction Γ -K of (a) 1-Bi-BL/Bi₂Se₃ ($h\nu = 20 \text{ eV}$), (b) first derivative of part a, to enhance the visibility of some bands. (c) DFT band structure of 1- Bi-BL/Bi₂Se₃. (d) Spectral weight of Bi-BL plus Bi₂Se₃ topmost two QLs. (e) Spectral weight of Bi-BL. (f) Spectral weight of Bi₂Se₃ topmost QL. (g) Spectral weight of Bi₂Se₃ QL second from the top.

preferentially removed as shown in Figure 4b. The Bi(I) sites become visible when Se atoms at the Se(I) site are removed in Figure 2c. With an increasing dosage of hydrogen atoms (Figure 4c), the outermost Se(I) atoms are completely depleted; the presence of Bi atoms at Bi(I) sites is more resistant to hydrogen etching. The vdW force between adjacent QLs is much weaker than the covalent chemical bonding between Bi(I) and Se(II), which promotes the reaction of hydrogen atoms with the Se(I') and Se(I) atoms situated in the vdW gap, and the bonding energy of H-Se has a local minimum.⁶⁹ The elimination of Se atoms at Se(I') and Se(I)sites can cause the formation of the Bi BL underneath the Se(II) level as shown in Figure 4d, as is the observation according to the STM images shown in Figure 2d,e. Additionally, before the Se(II) layer of the first QL layer was fully removed, the edge of the third QL has also been etched, and some Se(I) atoms near the step edge are partially removed, as shown in Figure 2a,d. Moreover, some Bi atoms might detach from Bi-Bi bonding and leap onto the Bi(I) level because of the small activation energy for diffusion,^{46,70} resulting in scattered Bi BL islands, as shown in the inset of Figure 2d. The enlarged part of Figure 2e can be understood as a consequence of coalescence of small openings via H etching. For dosage of hydrogen atoms beyond 1080 L, Se atoms in the first QL can be entirely removed; Bi BLs cover the Bi_2Se_3 surface, as shown in Figures 2f and 4e. It is worth pointing out that the Bi bilayer atop Bi_2Se_3 is also energetically favorable, according to the results of first principles calculations.⁴⁶

To improve our understanding of how the evolution of the topological surface states and of band dispersion is the layerdependent Bi BL formation, we measured the electronic structures of the n-Bi-BL/Bi₂Se₃ hybrid nanostructure using ARPES to compare with the band structure calculated with DFT. Figure 5a shows the ARPES spectra of single Bi-BL on Bi₂Se₃ along direction Γ -K, which corresponds to the STM sample with 1080 L H exposure (Figure 2f). The first derivative of the photoemission intensity is plotted to find the weak band dispersion, as shown in Figure 5b. Calculated band structures are displayed in Figure 5c. The APRES result is in excellent agreement with the calculation of band structure. In particular, several explicit features noted in the ARPES results of a Bi-BL/Bi₂Se₃ film are different form pristine Bi₂Se₃. In the single Bi-BL

Figure 6. Rashba splitting in Bi-BL/Bi₂Se₃. (a) $\langle S_y \rangle$ spin polarization spectral weight contributions from Bi cover layers along *G*-*K* (k_x). (b) $\langle S_x \rangle$ spin polarization spectral weight contributions from Bi cover layers along *G*-*M* (k_y). (c–e) Constant energy contours at energy $E = E_1 = 0.1$ eV with $\langle S_x \rangle$, $\langle S_y \rangle$, and $\langle S_z \rangle$, respectively.

case, the ARPES exhibit two well-separated Dirac points at the Γ point; one labeled with D_{TI} is located around -0.3 eV binding energy. The band velocity of charge carriers near D_{TI} is $\sim 2.58 \times 10^5$ m/s, which is about half of $\nu_{\rm F}$ in a bare Bi₂Se₃ film $(5.71 \times 10^5 \text{ m/s}, \text{ Figure 1d})$. The other point near the Fermi level is D_{Bi} with Fermi velocity (ν_F) ~ 4.34 × 10⁵ m/s. In addition, the band dispersion of new hole-like bands emerging around $k_{\parallel} \sim 0.45 \text{ Å}^{-1}$ at -0.8 eV binding energy is upward over $E_{\rm F}$. According to the DFT calculations (Figure 5d-g), we identify D_{Bi} as being derived from the crossing of Rashba splitting of extra hole-like bands. In order to deepen understanding of this splitting state, we extract the spin spectral weight in cover Bi-BL as shown in Figure 6. Momentum cuts (Figures 6a,b) as well as constant energy contours (Figure 6ce) show the clear one-to-one spin momentum locking feature, demonstrating a Rashba splitting in Bi-BL. Most importantly, we find the Rashba coupling constants ($\alpha = 2\Delta E/\Delta k$) of the splitting states up to 4.5 and 4.0 eV Å along k_x and k_y respectively (Figure 6a,b), which are to be compared with the value of 1.8 eV Å in Bi/Ge(111),⁷¹ 3.05 eV Å in Bi/Ag(111) surface alloy,⁷² and 3.8 eV Å in bulk BiTeI.⁷³ The remarkable giant Rashba splittings behave as non-negligible potentials for applications in spintronics. The origin of Rashba splitting is a result of large SOC and a strong potential gradient between Bi-BL and Bi2Se3 interface. Our results show that the spectral weight of D_{Bi} is mainly contributed from the Bi BL (Figure 5e). Contrary to D_{Bi} , the spectral weights of D_{TI} and the proximity in the linear band dispersion (nearly 100%) come from a second QL of Bi₂Se₃ as shown in Figure 5g. These signatures demonstrated a topological surface-band feature on the Bi2Se3 interface. The band shapes of the Bi2Se3 first QL notably change greatly (Figure 5f), resulting from the strong hybridization with the cover Bi-BL. The significant layer-layer interaction strongly modifies the original surface states of the Bi₂Se₃ first QL, causing the original topological protected Dirac

point as well as neighboring linear bands to move to a second QL to maintain a nontrivial band topology of the entire system. Since the 1-Bi-BL/Bi₂Se₃ hybrid structure can thus be regarded effectively as a Bi/1-QL metallic film covering the Bi₂Se₃, the bulk-boundary correspondence ensures the topological surface states will reappear on the surface of the Bi₂Se₃ (the surface of the original second QL of Bi_2Se_3). To our best knowledge, this perspective has never been reported in the n-Bi-BL/ Bi₂Se₃. ^{41,42,51} It is noteworthy that this new Dirac surface state is modified with decreased Fermi group velocity. In the 2D system, the topological edge state can be tuned by modifying the edge on-site potential as has been proposed in a freestanding Bi-BL film.³⁰ However, the described mechanism of Fermi velocity decreasing in Bi-BL/Bi₂Se₃ remains an open issue, and the interface effect in the 3D hybrid system is more complicated than the case in a pristine Bi-BL film. Here we propose a possible mechanism: the decrease of Fermi velocity may result from the interaction between surface states and quantum well states. The detailed discussion about the relation between the surface state movement and the decrease of Fermi velocity has been shown in Supporting Information (Figure S3). On increasing exposure of hydrogen, the ARPES data of 2-Bi-BL formation are presented in Figure S1 (Supporting Information). The D_{Bi} near $E_{\rm F}$ is still visible with $\nu_{\rm F} \sim 4.47 \times$ 10⁵ m/s, which is similar to that of 1-Bi-BL. ARPES data further show the band dispersion of extra hole-like bands arising upward from $k_{\parallel} \sim 0.4$ Å⁻¹ at -1.0 eV and sharply upward to $E_{\rm F}$. These extra states are contributed mainly from additional Bi cover layers, which are revealed by our 2-Bi-BL/Bi₂Se₃ model in Figure S2b (Supporting Information). It is to be noted that the slight deviation of electronic structure from ARPES and theory in 2-Bi-BL/Bi₂Se₃ might be due to the coexistence of 1-Bi-BL and 2-Bi-BL at the coverage. In particular, our DFT results predict that the Bi hole-like bands increase with increasing Bi BL thickness (Figure S2, Supporting Information).

CONCLUSION

From experiments in situ with STM, XPS, and ARPES combined with DFT calculations, we present evidence for Bi(111) bilayers with a uniform and flat long-range-ordered surface prepared with a top-down method using deliberate etching with atomic hydrogen. Our approach represents that the removal of Se begins from the top and bottom of a QL, leading to the selective formation of a Bi(111) bilayer in the vdW gap. The mechanism of the reaction of hydrogen with Bi₂Se₃ is elucidated from the evolution of the surface morphology and chemical variation. A large Rashba splitting is attributed to the large SOC and interface potential gradient between Bi(111) BL and Bi₂Se₃. Strong hybridization between the BL and the TI interface QL cause the topological surface states of Bi₂Se₃ to move toward a deeper QL to maintain a nontrivial band topology of the entire system. In addition, the thickness-dependent band structures indicated that the Bi holelike bands increase with increasing thickness of Bi BL. The selective hydrogen-etching technology might therefore work as a simple and convenient way to prepare 2D TI Bi(111) bilayers from 3D TI of Bi₂Se₃. We anticipate future experiments on topological signatures, such as transport measurements that probe the QSH effect via quantized universal conductance of the uniform and flat 2D TI Bi(111) bilayers.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b01908.

High-resolution ARPES result of 2-Bi-BL/Bi₂Se, DFT band evolution with increasing thickness of Bi-BL thin films, and plots of on-site potential artificially applied to the top-most first QL (V_{QL1}) of pristine Bi₂Se₃ and applied to the top-most first QL (V_{QL1}) and second QL (V_{QL2}) (PDF)

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Author Contributions

▲S.H.S. and P.Y.C. contributed equally to this work. S.H.S performed STM experiments with assistance from S.W.C. and H.Y.C. P.Y.C., W.C.C., and Y.T. performed the MBE growth. K.-D.T. and C.-M.C. performed ARPES experiments. P.Y.C., C.-H.W., and Y.-W.Y. performed XPS experiments. The theoretical analysis and computations were then performed by T.-R.C. All of the authors analyzed the data. S.H.S, P.Y.C., J.C.A.H., T.-R.C, and C.-M.C. wrote the manuscript. J.C.A.H., T.-R.C, and C.-M.C. were responsible for the overall research direction, planning, and integration among different research units.

Notes

The authors declare no competing financial interest.

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