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Large-Gap Magnetic Topological Heterostructure Formed by Subsurface Incorporation of a Ferromagnetic Layer

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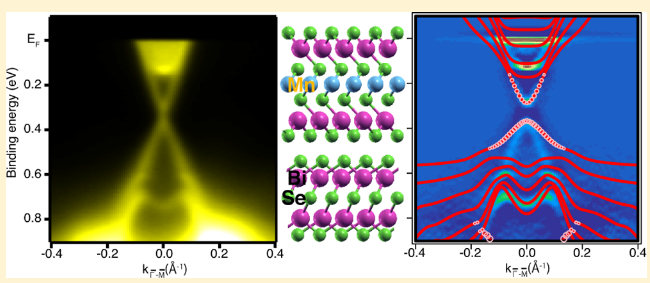
Supporting Information



ABSTRACT: Inducing magnetism into topological insulators is intriguing for utilizing exotic phenomena such as the quantum anomalous Hall effect (QAHE) for technological applications. While most studies have focused on doping magnetic impurities to open a gap at the surface-state Dirac point, many undesirable effects have been reported to appear in some cases that makes it difficult to determine whether the gap opening is due to the time-reversal symmetry breaking or not. Furthermore, the realization of the QAHE has been limited to low temperatures. Here we have succeeded in generating a massive Dirac cone in a $MnBi_2Se_4/Bi_2Se_3$ heterostructure, which was fabricated by self-assembling a $MnBi_2Se_4$ layer on top of the Bi_2Se_3 surface as a result of the codeposition of Mn and Se. Our experimental results, supported by relativistic *ab initio* calculations, demonstrate that the fabricated $MnBi_2Se_4/Bi_2Se_3$ heterostructure shows ferromagnetism up to room temperature and a clear Dirac cone gap opening of ∼100 meV without any other significant changes in the rest of the band structure. It can be considered as a result of the direct interaction of the surface Dirac cone and the magnetic layer rather than a magnetic proximity effect. This spontaneously formed self-assembled heterostructure with a massive Dirac spectrum, characterized by a nontrivial Chern number $C = -1$, has a potential to realize the QAHE at significantly higher temperatures than reported up to now and can serve as a platform for developing future "topotronics" devices.

KEYWORDS: *Topological insulators, magnetism, massive Dirac cone, quantum anomalous Hall effect*

Classification of materials and phases based on the "topological properties" of the system has become one of the most extensively studied research fields in physics and

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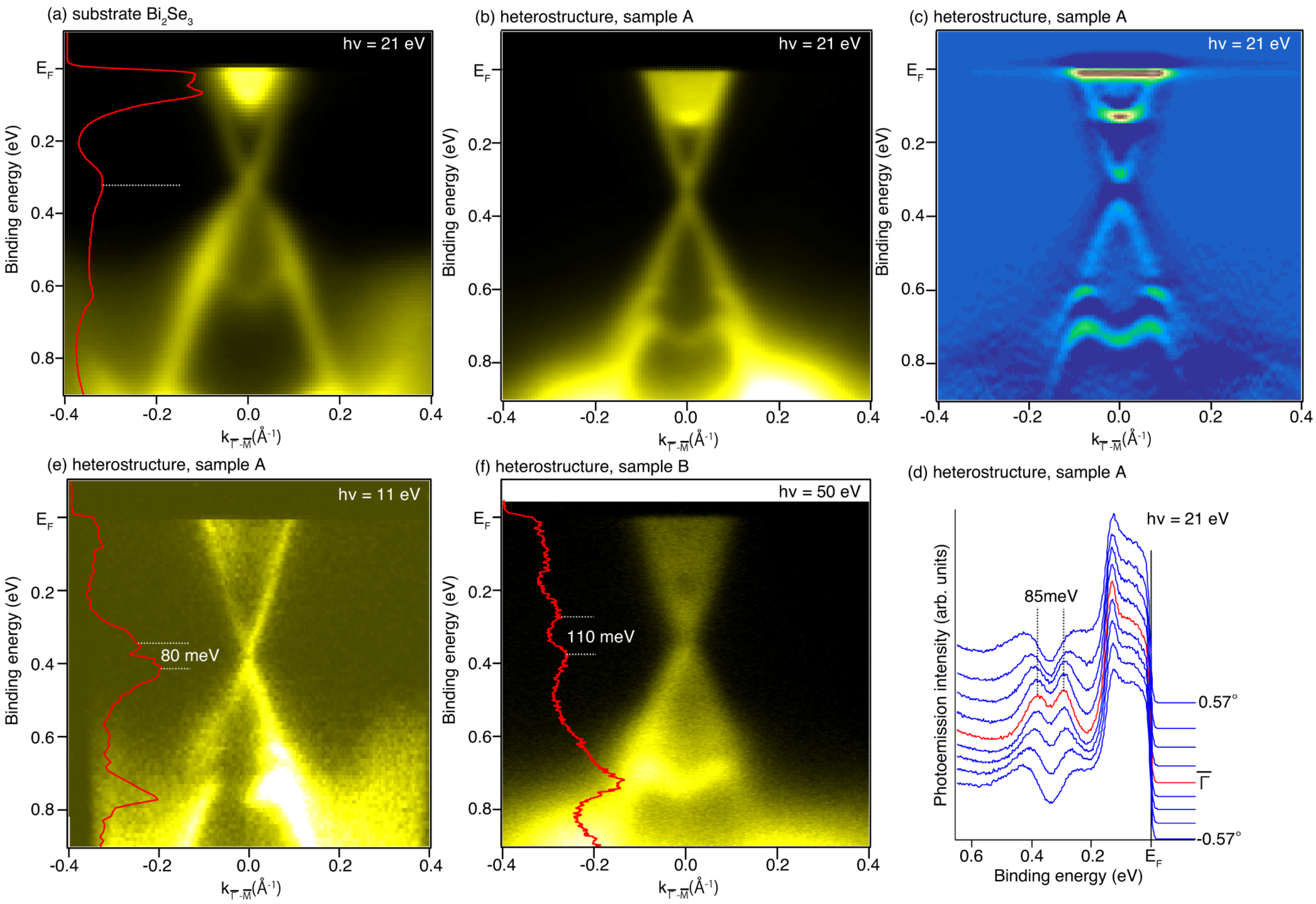

Figure 1. (a) Band dispersion of the substrate Bi_2Se_3 film measured along the $\bar{\Gamma}-\bar{M}$ direction taken at $h\nu$ = 21 eV. The red line shows the energy distribution curve (EDC) at the $\bar{\Gamma}$ point. (b) Band dispersion of the heterostructure for sample A measured along the $\bar{\Gamma}-\bar{M}$ direction taken at $h\nu$ = 21 eV. (c) The second derivative with respect to the energy of the band dispersion in (b). (d) Raw spectra (EDCs) near the $\bar{\Gamma}$ point of the band dispersion in (b). The gap size of the Dirac cone is 85 meV. (e) Band dispersion of the heterostructure for sample A measured along the $\bar{\Gamma}-\bar{M}$ direction taken at $h\nu$ = 11 eV. The gap size of the Dirac cone is 80 meV. The red line shows the EDC at the $\bar{\Gamma}$ point. (f) Band dispersion of the heterostructure for sample B measured along the $\bar{\Gamma}-\bar{M}$ direction taken at $h\nu$ = 50 eV. The gap size of the Dirac cone is 110 meV. The red line shows the EDC at the $\bar{\Gamma}$ point. All the measurements were performed at 30 K.

was the topic for the Nobel prize in physics in 2016.[1] Topological insulators (TIs) are insulating materials that have metallic surface states, whose electron spins are locked to their momentum.[2,3] In the simplest case, the surface states are helical Dirac Fermions and the Dirac point is robust due to the protection by time-reversal symmetry. When the time-reversal symmetry is broken in TIs, novel quantum phenomena have been predicted to occur including the formation of magnetic monopoles,[4] the quantum anomalous Hall effect (QAHE),[5] and the topological magnetoelectric effect.[6]

In terms of the electronic structure, a magnetic TI is expected to host a massive Dirac cone with a band gap. Many researches have been performed to induce magnetism in TIs by magnetic impurity doping when growing thin films.[7,8] Although it seemed that this was the most efficient way with the successful observation of the QAHE in Cr- or V-doped $(Bi,Sb)_2Te_3$ thin films,[8−10] the precise quantization of the Hall resistance at zero field is still only limited to low temperature (10−100 mK). The temperature for the realization of the QAHE (T_{QAHE}) depends on the Curie temperature as well as the size of the Dirac cone gap of the system. Up to now, the main obstacle in enhancing T_{QAHE} is an inhomogeneous distribution of magnetic atoms over the TI film that results in strong fluctuations of the magnetic energy gap.[11,12] Modulation doping was shown to increase T_{QAHE} and the QAHE was observed at 2 K for Cr-doped $(Bi,Sb)_2Te_3$ thin films when the magnetic-doped layer was placed 1 nm below the surface.[13] A recent theoretical work suggests that this can be enhanced by V and I codoping of Sb_2Te_3.[14]

Another drawback of the magnetically doped systems is that there has been no direct observation of the massive Dirac cone for the samples that show the QAHE using angle-resolved photoemission spectroscopy (ARPES).[15] With local probes such as scanning tunneling spectroscopy (STS), an inhomogeneous Dirac cone gap was observed for Cr-doped $(Bi,Sb)_2Te_3$.[11] However, for V-doped Sb_2Te_3, it was reported that impurity states will reside within the Dirac cone gap, and as a result, the density of states will look gapless.[16] Moreover, impurity bands will emerge near the Dirac point, and it was reported that a massive Dirac cone can arise even due to a nonmagnetic origin for impurity-doped Bi_2Se_3 films with ARPES.[17] Thus, one can say that magnetic impurity doped TI films are not promising in terms of (i) enhancing T_{QAHE} to the region where application becomes possible and (ii) clearly observing the gapped Dirac cone as a result of the time-reversal symmetry breaking in a macroscopic scale.

An alternative way to induce magnetism in TIs is to make a heterostructure of TIs and magnets. Such systems are also used

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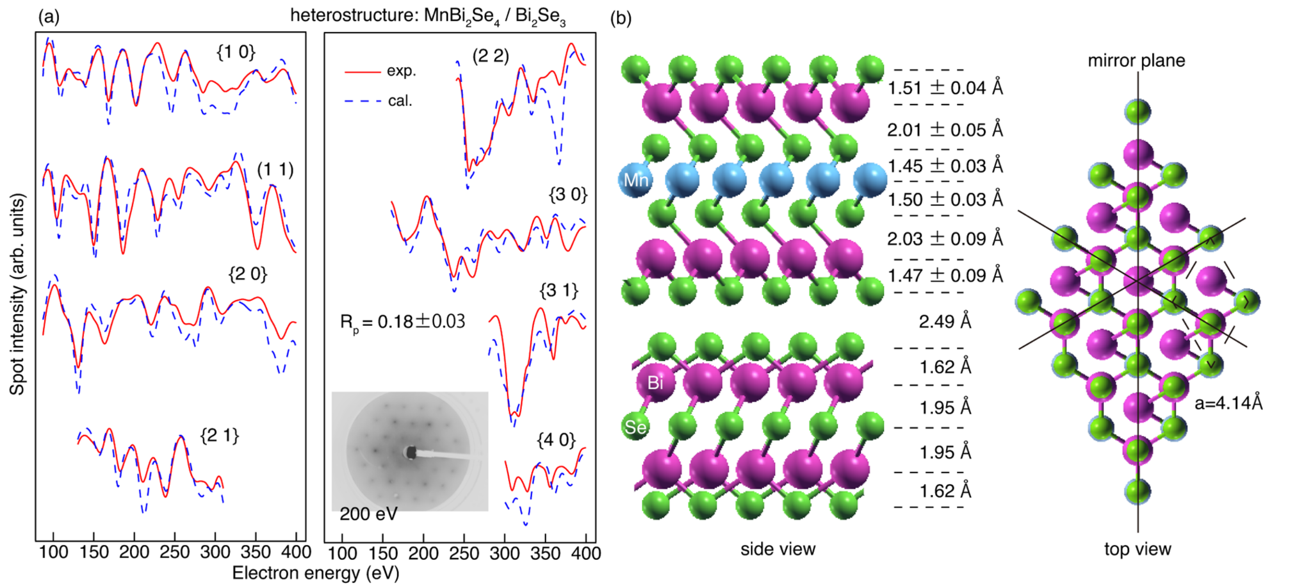

Figure 2. (a) Experimental *IV* spectra of LEED spots measured at 100 K for the heterostructure (red solid lines), and the calculated spectra of the optimized model shown in (b) (blue dotted lines). The inset shows the LEED pattern at 200 eV. (b) Cross-sectional (left) and top (right) view of the optimized model of the heterostructure, which turns out to be $MnBi_2Se_4/Bi_2Se_3$. Blue, pink, and green atoms represent Mn, Bi, and Se, respectively. The solid lines show the mirror plane and the dotted parallelogram shows the unit cell.

in experiments to observe the surface-state spin transport.[18−21] However, there has not been a direct observation of the QAHE as well as the existence of a gapped Dirac cone at the interfaces in these heterostructures. One reason for this is the absence an atomically sharp interface that makes the gap small and difficult to observe, which should be also responsible for the low spin-charge conversion efficiency. Even in some cases with a sharp interface (EuS/Bi_2Se_3), the Dirac cone gap was shown not to be related with the magnetic proximity effect,[22] although magnetization measurements showed evidence of a magnetic interaction.[23] In another case of $MnSe/Bi_2Se_3$, it was shown from *ab initio* calculations that states other than the gapped Dirac cone will cross E_F[24] and make the QAHE impossible to realize. However, the measured band structure was completely different from the calculation, but no clear explanation was given.[25] Thus, the interplay between the topological properties and magnetism in an ordered layered system needs to be examined further.

In the present study, we take advantage of self-organization to produce an ideal system of a magnetic insulator/TI heterostructure, which is formed spontaneously as a hexagonal $MnBi_2Se_4$ septuple layer (SL) on the basis of the topmost quintuple layer (QL) of Bi_2Se_3 film under Mn and Se codeposition. Due to the ferromagnetism of $MnBi_2Se_4$ up to room temperature as revealed by superconducting quantum interference device (SQUID) and X-ray magnetic circular dichroism (XMCD) measurements, the Dirac cone becomes massive with a gap size of ∼100 meV. First-principles calculations show that the calculated Chern number is $C = -1$, and the heterostructure is identified as a quantum anomalous Hall phase. Our results not only show the first example of a clear Dirac cone gap opening at the ferromagnet/TI interface but imply that this should be a suitable system to realize the QAHE at higher temperatures than previously reported by tuning the Fermi level as well as to develop novel devices based on the topological magnetoelectric effect.

Figure 1a shows the band dispersion of the Bi_2Se_3 thin film, which was used as the substrate for the heterostructure formation. The well-known Dirac cone of the surface states in the bulk band gap can be seen together with the bulk conduction band at the Fermi level due to the unintentional doping. The Dirac point is recognized as shown in the energy distribution curve (EDC) at the $\bar{\Gamma}$ point (red line). Figure 1b shows the band structure of the heterostructure (sample A) after Mn and Se were codeposited on Bi_2Se_3. It was measured immediately after cooling down the sample. A clear gap opening is observed at the Dirac point. This becomes more prominent by making the second derivative with respect to the energy of the image in Figure 1b, which is shown in Figure 1c. The gap size is deduced as ∼85 meV from the EDCs in Figure 1d. A slightly smaller gap is observed when the photon energy is changed to 11 eV, as shown in Figure 1e. The estimated gap size is ∼80 meV, which is nearly the same as that shown in Figure 1d. It can also be noticed that the midpoint of the energy gap has shifted down by about 70 meV from Figure 1b−d to Figure 1e, due to the band bending near the surface caused by the residual gas or defect formation[26,27] since Figure 1e was measured 12 h after Figure 1b−d. The band dispersion images taken with other photon energies for sample A are shown in Figure S1. Even though the gap exists irrespective of the Fermi level position, the gap size slightly changes depending on the measurement condition. However, there is no correlation between the midgap position and the gap size. Figure 1f shows the band dispersion image of a different sample (sample B) taken at $h\nu$ = 50 eV just after cooling down the sample posterior to the preparation. The gap size is ∼110 meV, larger than that for sample A although the midpoint of the gap is nearly the same. We have also measured the gap size for other samples, and the gap value is in the range of 75−120 meV when the Dirac point is located at the binding energy of 0.31−0.39 eV, although there is no correlation between the two quantities. We conclude that when Mn and Se are codeposited on Bi_2Se_3 and a heterostructure is formed, the Dirac cone becomes gapped. At first glance, it should be due to the magnetic proximity effect from antiferromagnetic MnSe.

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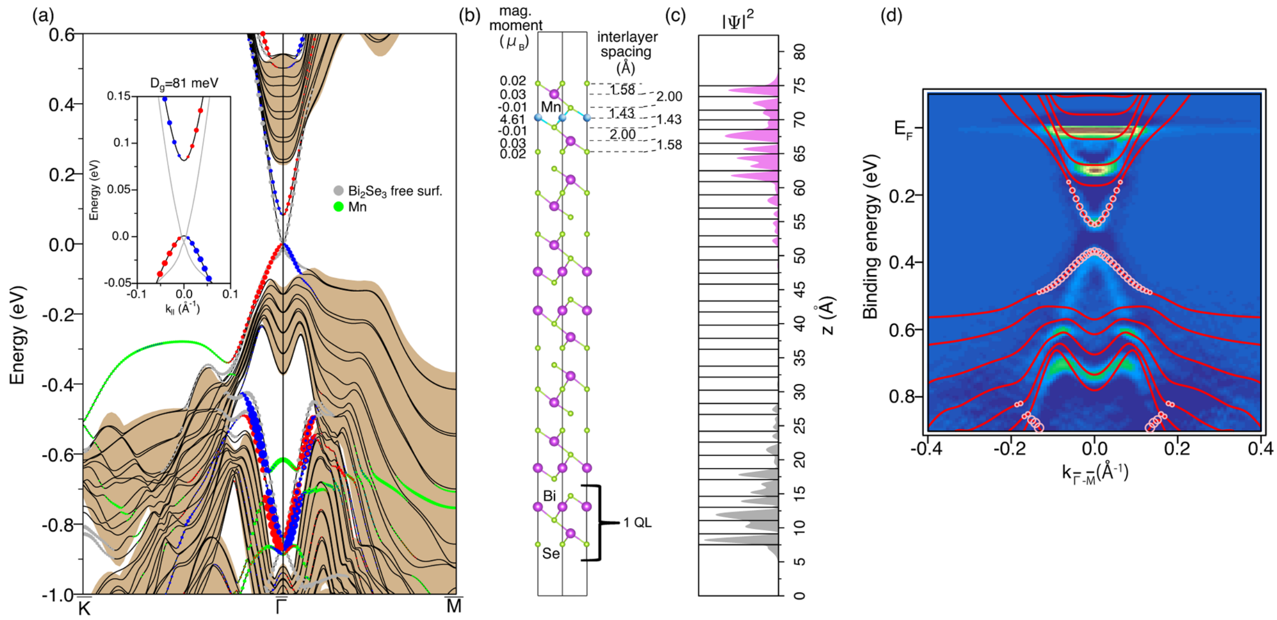

Figure 3. (a) Calculated band dispersion of a $MnBi_2Se_4$/6QL Bi_2Se_3 heterostructure. The states marked in red and blue are localized at the topmost SL and the next Bi_2Se_3 QL and spin-polarized in the in-plane direction perpendicular to the wavenumber (positive and negative, respectively). The states marked in green are the ones mostly localized at $MnBi_2Se_4$ SL and labeled "Mn". The states localized at the bottom surface of the slab are indicated in gray. The shaded area shows the bulk band projection of Bi_2Se_3. The inset shows a close-up of the Dirac state dispersion. A gap of 81 meV is found for the Dirac cone at the top surface. (b) The real space atomic configuration used in the calculation together with the interlayer spacings and layer-resolved magnetic moments. (c) Wave function ($|\Psi|^2$) plot for the gapped Dirac state at the top surface (violet) and that at the bottom surface (gray), respectively. (d) The calculated band dispersion overlapped with the experimental data of Figure 1c. Pink circles show the states localized in the SL.

However, there is one contradictory point about this band dispersion of the heterostructure. According to *ab initio* calculations,[24] the band dispersion of a MnSe/Bi_2Se_3 heterostructure should have the following characteristics: (i) a massive Dirac cone with a gap of 8.5 meV and (ii) other metallic states in the Bi_2Se_3 bulk band gap. In our experimental data, we do not find any additional states in the Dirac state energy region. Moreover, the gap size is an order of magnitude larger than that predicted in the calculation. Therefore, the calculation and the experiment are not consistent with each other. Various factors may be responsible for this inconsistency, such as the difference in the interface structure or the thickness of the MnSe layers. We have therefore performed structure analyses of the heterostructure based on the LEED *IV* technique to resolve this inconsistency.

Figure 2a shows the experimentally observed *IV* curves (red solid lines). To reproduce these curves, we have first assumed the MnSe/Bi_2Se_3 heterostructure that is expected from the sample preparation method. However, we could not obtain R-factor (R_p) values smaller than 0.4. Thus, it was proven that the heterostructure we have fabricated was not MnSe/Bi_2Se_3. We tried other structures and finally found one that was in striking agreement with the experimental LEED *IV* curves. The calculated *IV* curves for the optimized structure are shown by the blue-dotted lines in Figure 2a. The agreement between the two curves is excellent with $R_p = 0.18 \pm 0.03$. The structure thus determined is shown in Figure 2b. What is remarkable about this structure is that the deposited Mn and Se are not on top of the Bi_2Se_3 substrate, but they are incorporated inside the topmost QL of Bi_2Se_3. So we can say that a $MnBi_2Se_4$ SL spontaneously forms on top of Bi_2Se_3 by self-organization. Although the microscopic mechanism of MnSe bilayer immersion into the QL is not clear, our calculations show that the $MnBi_2Se_4$ SL is 630 meV energetically more favorable as compared to the MnSe bilayer (BL)/Bi_2Se_3 QL interface. $MnBi_2Se_4$ in the bulk form is reported to have the monoclinic structure with $C2/m$ symmetry. It is shown to be a narrow gap semiconductor and antiferromagnetic with $T_{Neel} \approx 14$ K.[28] However, the $MnBi_2Se_4$ SL that we have fabricated has a hexagonal structure and is a semiconductor with a gap of ~0.4 eV (Figure S3).

The electronic structure of the heterostructure was calculated based on the determined atomic structure of Figure 2b. Namely, a six QL film of Bi_2Se_3 was sandwiched between $MnBi_2Se_4$ and vacuum. The interlayer spacing values obtained after structural relaxation of the heterostructure and shown in Figure 3b are in excellent agreement with the experimentally determined values shown in Figure 2b. We found that the spin structure with the Mn magnetic moment pointing out-of-plane is 0.2 meV energetically more favorable than the one with in-plane spin polarization, and the magnetic moment of Mn was found to be 4.61 μ_B (Figure 3b). The calculated band dispersion is shown in Figure 3a. The red and blue points correspond to the states with in-plane spin polarization perpendicular to the wavenumber (positive and negative, respectively) that are localized at the topmost SL and the neighboring QL (refer to the Supporting Information for the experimental results of the Dirac cone spin-polarization). Near the Fermi level, the massless Dirac cone of pristine Bi_2Se_3 at the bottom surface can be found (gray points and gray line in inset) together with the massive Dirac state with a gap $D_g = 81$ meV at the top surface. The "gray" band can be a good reference for tracking the changes in the Dirac state. As can be seen, the lower part of the Dirac cone of the gapped state shows almost no change in the energy position, and the gap is formed by shifting up the upper branch. The calculations performed for a

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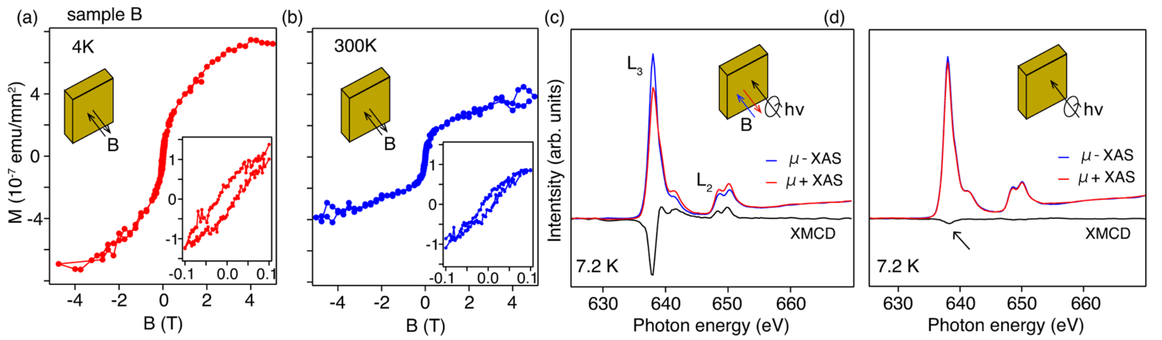

Figure 4. (a,b) Magnetization curves measured with SQUID for the Se-capped sample B taken at 4 K (a) and at 300 K (b), respectively. The magnetic field was applied perpendicular to the sample surface. The inset shows the close-up near zero-field. Clear hysteresis loops can be observed both at 4 and 300 K. (c) X-ray absorption spectra (XAS) at 7.2 K for a circularly polarized incident light when a ±5 T magnetic field was applied along the surface-normal direction. μ_+ and μ_- correspond to the spectrum obtained at +5 T and -5 T, respectively. The corresponding XMCD spectra is also shown. The Se capping layer was removed by annealing the sample in UHV. (d) Same as that in (c) but measured at zero field. A remanent XMCD signal can be observed (shown by the arrow).

symmetric heterostructure, where Bi_2Se_3 is sandwiched between two $MnBi_2Se_4$ SLs, result in the same value of the Dirac cone gap. Figure 3d shows this calculated spectrum overlapped with the experimental result (the calculation was rigidly shifted by −0.38 eV to fit to the experimental E_F). The agreement between the two is excellent with exception of flatter dispersion in the bottom part of the Dirac cone in the calculation whereas the gap size in the Dirac cone, as well as fine structures other than the Dirac cone, are reproduced. The green points in Figure 3a are states localized at the topmost SL and labeled "Mn" because it has the maximum contribution from the Mn p_z orbitals. They are located along the $\bar{\Gamma}-\bar{K}$ direction in the Bi_2Se_3 bulk band gap and a band that resembles this is also found in the calculated dispersion of the free-standing $MnBi_2Se_4$ SL (Figure S3). This was actually observed experimentally when we performed ARPES measurements along the $\bar{\Gamma}-\bar{K}$, as shown in Figure S9a. Altogether, the calculation reproduces the experimentally observed band structure nicely, and we are sure that the heterostructure we have fabricated is $MnBi_2Se_4/Bi_2Se_3$. Moreover, one can say that the mass acquisition of the Dirac cone is not due to a magnetic proximity effect because the Dirac state and the magnetic layer are both at the topmost SL (70% of the Dirac state is localized in the SL, see Figure 3c) We should rather say that this is a "direct interaction" between the magnetic layer and the surface Dirac cone, since they overlap in real space and some part of the wave-function of the Dirac cone is within the Mn layers. The original Dirac cone of Bi_2Se_3 has been pushed up to the newly formed $MnBi_2Se_4$ capping layer, which has been discussed previously for other topological-insulator based heterostructures.[29] This is the reason why there is a large gap of ~80 meV at the Dirac point in contrast to the case of MnSe/Bi_2Se_3 where a magnetic proximity effect was considered.[24]

The gapped Dirac state has a potential to realize the QAHE. The quantized Hall conductance $\sigma_{yx} = Ce^2/h$ is related to the topological characteristic of the band structure known as the Chern number C.[30] Our calculations show that the gapped spectrum of the $MnBi_2Se_4/Bi_2Se_3$ heterostructure is characterized by the Chern number $C = -1$, which defines the obtained heterostructure unambiguously as a quantum anomalous Hall phase. To confirm the topological character of the heterostructure spectrum, we artificially decreased the spin−orbit interaction strength λ and found that it leads to the gap narrowing and its closing at $\lambda/\lambda_0 \approx 0.75$ (see Figure S4). Upon further decrease of the spin−orbit interaction strength, the gap reopens and the system becomes a topologically trivial insulator.

Next, we have tried to experimentally verify the absence of time-reversal symmetry in the heterostructure as the calculation suggests. Figure 4a,b shows the magnetization curves measured with SQUID for the Se-capped sample B taken at 4 K (a) and at 300 K (b), respectively. The magnetic field was applied perpendicular to the sample surface. (The data for the in-plane magnetization can be found in Figure S7). In order to display the situation near zero-field clearly, we show in the inset the close-up for −0.1 to 0.1 T. There is a vivid hysteresis loop both at 4 and 300 K, demonstrating the ferromagnetic nature of the heterostructure.[31] Actually, the gapped Dirac cone can also be observed at room temperature (Figure S2), and thus, the Curie temperature is confirmed to be above 300 K also from ARPES. We also performed XMCD measurements after removing the Se cap in UHV to make sure that the Se cap is not affecting the magnetic properties. Figure 4c shows the X-ray absorption (XAS) spectra at the Mn L edge measured at 7.2 K for a circularly polarized incident light when a ±5 T magnetic field was applied along the surface-normal direction. μ_+ and μ_- correspond to the spectrum obtained at +5 T and −5 T, respectively. The corresponding XMCD spectrum is also shown, and there is a clear signal. The quantitative analysis of the XMCD measurements using the sum-rule is discussed in the Supplementary Information, see Figure S5. The measurements were also performed at remanence (0 T applied magnetic field), namely, the signal was obtained after switching off the ±5 T magnetic field applied perpendicular to the surface (Figure 4d). Although weak (the peak at the L_3 edge is ~7% compared to the data of Figure 4c), we still can notice the XMCD signal (the arrow in Figure 4d), and this confirms that the system is ferromagnetic. We believe that the SQUID data of Figure 4a,b and that obtained by XMCD in Figures 4c,d are both showing the ferromagnetism of the Mn layer despite the different probing depth of the two measurements since it can be the only source of ferromagnetism in the present heterostructure system.

The heterostructure we have fabricated demonstrates various advantages compared to previously studied quantum anomalous Hall systems. First, it forms spontaneously by depositing Mn and Se on top of Bi_2Se_3. We have done this using thin films, but in principle, it should also be possible to do this for single

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crystals or even thinner films. This is in contrast to the extensively studied systems with an intentional magnetic impurity doping[7−9,16,17] in which fine-tuning of the impurity concentration is needed to achieve a long-range magnetic order.[32]

Second, in our samples, we have an ideal situation where the Dirac cone and the magnetic layer interact strongly due to the spatial overlap of the respective wave functions, thus leading to a large magnetic gap but with minimal effects on other bands. This is in contrast to heterostructures that utilize the magnetic proximity effect.[22−24]

Third, our samples are free from inhomogeneity since the structure was clearly determined by LEED measurements. This allowed us to observe a clear Dirac cone gap with ARPES and assign its origin unambiguously as due to the time-reversal symmetry breaking. Recalling that the presence of the impurity states makes it difficult to determine the gap opening in the Dirac cone as well as its origin,[16,17] this is a merit. Furthermore, the clear gap opening in ARPES means that our heterostructure does not show strong fluctuations of the magnetic energy gap.[11]

Finally, the Curie temperature of the heterostructure is above room temperature. Furthermore, the Dirac cone gap is larger than the thermal fluctuation at room temperature. Therefore, we can expect to observe the QAHE for our samples at higher temperatures than those previously reported[8−10] by moving the Fermi level into the induced gap either chemically[7] or by gating.[8,10,32] So our heterostructure may be used in application for developing "topotronics" devices.

Experimental and Calculation Methods. The heterostructure samples were prepared by molecular beam epitaxy in ultrahigh vacuum (UHV) chambers equipped with a reflection-high-energy electron diffraction (RHEED) system. First, a clean Si(111)-7 × 7 surface was prepared on an *n*-type substrate by a cycle of resistive heat treatments. The Si(111)β $\sqrt{3} \times \sqrt{3}$-Bi surface was formed by 1 ML (7.83×10^{14} cm^{-2}) of Bi deposition on the 7 × 7 surface at 620 K monitored by RHEED. Then Bi was deposited on the β $\sqrt{3} \times \sqrt{3}$-Bi structure at ∼200 °C in a Se-rich condition. Such a procedure is reported to result in a smooth epitaxial film formation with the stoichiometric ratio of Bi/Se = 2:3.[33,34] The grown Bi_2Se_3 films were annealed at ∼240 °C for 5 min. The thickness of the Bi_2Se_3 films in this work is ∼15 QL, which does not show the gap opening in the Dirac cone due to finite-size effects,[34,35] as shown in Figure 1a. Finally, Mn was deposited on Bi_2Se_3 in a Se-rich condition at ∼240 °C. As reported in ref 25, this results in a flat film formation, which was believed to be a heterostructure of MnSe/Bi_2Se_3.

ARPES and SARPES measurements were performed *in situ* after the sample preparation. The ARPES measurements were performed at BL-5U and 7U of UVSOR-III using *p*-polarized photons in the energy range of 30−65 and 7.5−28 eV, respectively.[36] All the data shown were taken at 30 K unless otherwise indicated. The energy and angular resolutions were 15 meV and 0.25°, respectively. The SARPES measurements were performed at BL-9B of HiSOR using *p*-polarized photons in the energy of 18−21 eV at 30 K.[37] In some of the measurements, a magnetic field as large as ∼0.1 T was applied to the sample. The energy and angular resolutions were 30 meV and 0.75°, respectively.

LEED measurements were also performed *in situ* after the sample formation in another UHV chamber. The LEED patterns with incident energy from 80 to 400 eV were recorded in steps of 1 eV by a digital CCD camera at 100 K. *IV* curves of 14 inequivalent diffraction spots were obtained. In order to determine the surface structure, we calculated the *IV* curves in the tensor LEED to fit the experimental *IV* curves using the SATLEED package of Barbieri/Van Hove[38] and minimized Pendry's R-factor (R_p). As shown in Figure 2b, each atomic layer was treated differently according to their environments. The in-plane lattice constant of the heterostructure was determined from positions of the LEED spots as well as the RHEED spots and was the same with that of Bi_2Se_3. Angular momentum up to 17 (l_{max} = 17) was taken into account because of the strong scattering of the heavy Bi atom (Z = 83). Considering the mean penetration depth of the incident electrons of ∼10 Å, only the topmost seven surface layers were allowed to relax, and we used the bulk Bi_2Se_3 parameters for the layers beneath. In search of the optimal structure, the Debye temperature of each atom was changed in steps of 10 K from 50 K up to 300 K. If MnSe grew on Bi_2Se_3, it should have the *p*3*m*1 symmetry. However, the symmetrically inequivalent spots, such as (1,0) and (0,1), exhibited almost the same *IV* curves. Since this was also seen for the pristine Bi_2Se_3 LEED patterns, it probably comes from the fact that there are twin domains on the surface that are related by a 180° rotation. The superposition of the two domains should lead to the apparent 2-fold symmetry. Taking this double-domain surface into account, we took the average of the *IV* curves both in the calculation and in the experimental data such that {h,k} is the average of (h,k) and (k,h) spots (see Figure 2a). Note that spots having the same mirror indices of h and k do not need averaging.

For the SQUID measurements, the fabricated samples were capped with ∼15 nm of Se before taking it out of the UHV chamber, and a commercial MPMS-52 system (Quantum Design) was used. The diamagnetic contribution of the Si substrate was derived from the field-dependent magnetization curves at room temperature and subtracted from all data.

XMCD measurements were performed at BL-4B of UVSOR-III with circularly polarized X-ray radiation (positive helicity with the polarization of 0.6) at 7.2 K and a magnetic field as high as ±5 T was applied to the sample.[39] Instead of changing the photon polarization, we reversed the direction of the magnetic field to derive the XMCD spectra. As shown in Figure 4c, + (−) magnetic field corresponds to the direction antiparallel (parallel) to the direction of the photon incidence. The measurements were first performed for the samples with Se-capping. After measuring, the Se-capped samples were annealed at ∼240 °C to remove the capping layers. LEED observations showed a clear recovery of the 1 × 1 surface periodicity for the cap-removed samples.

For structural optimization and electronic band calculations we used the Vienna Ab Initio Simulation Package[40,41] with generalized gradient approximation (GGA-PBE)[42] to the exchange-correlation potential. The interaction between the ion cores and valence electrons was described by the projector augmented-wave method.[43,44] The Hamiltonian contains scalar relativistic corrections, and the spin−orbit interaction (SOI) is taken into account by the second variation method.[45] To correctly describe the highly correlated Mn-d electrons we include the correlation effects within the GGA+U method.[46] The in-plane lattice constant of the heterostructure was fixed to that of Bi_2Se_3. DFT-D3 van der Waals corrections[47] were applied for accurate structure optimization. The Chern number was calculated for a symmetric $MnBi_2Se_4$/5QL-Bi_2Se_3/

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$MnBi_2Se_4$ slab by using the method based on tracking the evolution of hybrid Wannier functions realized in Z2 Pack.[48]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b00560.

Additional details on ARPES, SARPES, *ab inito* calculations, SQUID, and XMCD measurements (PDF)

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Notes

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