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 MnBi2Se4/Bi2Se3 heterostructure, which was fabricated by self-assembling a MnBi2Se4 layer on top of the Bi2Se3 surface as a result of the codeposition of Mn and Se. Our experimental results, supported by relativistic ab initio calculations, demonstrate that the fabricated MnBi2Se4/Bi2Se3 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
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.\(^4\) When the time-reversal symmetry is broken in TIs, novel quantum phenomena have been predicted to occur including the formation of magnetic monopoles,\(^5\) the quantum anomalous Hall effect (QAHE),\(^6\) and the topological magnetoelectric effect.\(^7\)

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)\(_2\)Te\(_3\) thin films when the magnetic-doped layer was placed 1 nm below the surface.\(^8\) A recent theoretical work suggests that this can be enhanced by V and I codoping of Sb\(_2\)Te\(_3\).\(^14\) 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)\(_2\)Te\(_3\).\(^11\) However, for V-doped Sb\(_2\)Te\(_3\), 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\(_2\)Se\(_3\) films with ARPES.\(^17\) Thus, one can say that magnetic impurity doped TI films are not promising in terms of (i) enhancing \(T_{\text{QAHE}}\) 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

Figure 1. (a) Band dispersion of the substrate Bi\(_2\)Se\(_3\) film measured along the \(\Gamma\)-\(\bar{M}\) direction taken at \(h\nu = 21\) eV. The red line shows the energy distribution curve (EDC) at the \(\Gamma\) point. (b) Band dispersion of the heterostructure for sample A measured along the \(\Gamma\)-\(\bar{M}\) 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 \(\Gamma\) 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 \(\Gamma\)-\(\bar{M}\) 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 \(\Gamma\) point. (f) Band dispersion of the heterostructure for sample B measured along the \(\Gamma\)-\(\bar{M}\) 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 \(\Gamma\) point. All the measurements were performed at 30 K.
magnetization measurements showed evidence of a magnetic
interference device (SQUID) and X-ray magnetic circular
dichroism (XMCD) measurements, the Dirac cone becomes
visible at room temperature as revealed by superconducting quantum
Hall effect experiments. 

However, there has not been a direct observation of the QAHE
eff in experiments to observe the surface-state spin transport.18–21
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 MnBi2Se4 septuple layer (SL) on the basis of the topmost quintuple layer (QL) of Bi2Se3 film under Mn and Se codeposition. Due to the ferromagnetism of MnBi2Se4 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 Bi2Se3 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 Γ point (red line). Figure 1b shows the band structure of the heterostructure (sample A) after Mn and Se were codeposited on Bi2Se3. 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 to Figure 1e, due to the band bending near the surface caused by the residual gas or defect formation22–24 since Figure 1e was 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 $hν = 50$ 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 Bi2Se3 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.
Figure 3. (a) Calculated band dispersion of a MnBi₂Se₄/6QL Bi₂Se₃ heterostructure. The states marked in red and blue are localized at the topmost SL and the next Bi₂Se₃ 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 MnBi₂Se₄ 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 Bi₂Se₃. 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 (|Ψ|^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, the band dispersion of a MnSe/Bi₂Se₃ 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 Bi₂Se₃ 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/Bi₂Se₃ heterostructure that is expected from the sample preparation method. However, we could not obtain R-factor (Rₚ) values smaller than 0.4. Thus, it was proven that the heterostructure we have fabricated was not MnSe/Bi₂Se₃. 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 Rₚ = 0.18 ± 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 Bi₂Se₃ substrate, but they are incorporated inside the topmost QL of Bi₂Se₃. So we can say that a MnBi₂Se₄ SL spontaneously forms on top of Bi₂Se₃ by self-organization. Although the microscopic mechanism of MnSe bilayer immersion into the QL is not clear, our calculations show that the MnBi₂Se₄ SL is 630 meV energetically more favorable as compared to the MnSe bilayer (BL)/Bi₂Se₃ QL interface. MnBi₂Se₄ 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 T₆₉ ≈ 14 K. However, the MnBi₂Se₄ 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 Bi₂Se₃ was sandwiched between MnBi₂Se₄ 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 μₖ (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 Bi₂Se₃ at the bottom surface can be found (gray points and gray line in inset) together with the massive Dirac state with a gap Δₖ = 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
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).

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. 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 L3 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 Bi2Se3. We have done this using thin films, but in principle, it should also be possible to do this for single
crystals or even thinner films. This is in contrast to the extensively studied systems with an intentional magnetic impurity doping\textsuperscript{7–9,16,17} in which fine-tuning of the impurity concentration is needed to achieve a long-range magnetic order.\textsuperscript{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.\textsuperscript{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,\textsuperscript{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.\textsuperscript{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\textsuperscript{45–47} by moving the Fermi level into the induced gap either chemically\textsuperscript{7} or by gating.\textsuperscript{3,10,32} 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 \times 7 surface was prepared on an n-type substrate by a cycle of resistive heat treatments. The Si(111)β √3 \times √3-Bi surface was formed by 1 ML (7.83 \times 10^{14} \text{cm}^{-2}) of Bi deposition on the 7 \times 7 surface at 620 K monitored by RHEED. Then Bi was deposited on the β √3 \times √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.\textsuperscript{33,34} The grown Bi\textsubscript{3}Se\textsubscript{2} films were annealed at ~240 °C for 5 min. The thickness of the Bi\textsubscript{3}Se\textsubscript{2} films in this work is ~15 QL, which does not show the gap opening in the Dirac cone due to finite-size effects,\textsuperscript{35} as shown in Figure 1a. Finally, Mn was deposited on Bi\textsubscript{3}Se\textsubscript{2} 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 Mn\textsubscript{3}Se\textsubscript{2}/Bi\textsubscript{3}Se\textsubscript{2}.

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 eV and 7.5–28 eV, respectively.\textsuperscript{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.\textsuperscript{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\textsuperscript{38} and minimized Pendry’s R-factor (R). 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\textsubscript{3}Se\textsubscript{2}. Angular momentum up to 17 (l\textsubscript{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\textsubscript{3}Se\textsubscript{2} 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\textsubscript{3}Se\textsubscript{2}, it should have the p3m1 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\textsubscript{3}Se\textsubscript{2}, 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.\textsuperscript{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 \times 1 surface periodicity for the cap-removed samples.

For structural optimization and electronic band calculations we used the Vienna Ab Initio Simulation Package\textsuperscript{40,41} with generalized gradient approximation (GGA-PBE)\textsuperscript{62} to the exchange-correlation potential. The interaction between the ion cores and valence electrons was described by the projector augmented-wave method.\textsuperscript{43,44} The Hamiltonian contains scalar relativistic corrections, and the spin–orbit interaction (SOI) is taken into account by the second variation method.\textsuperscript{45,46} To correctly describe the highly correlated Mn-d electrons we include the correlation effects within the GGA+U method.\textsuperscript{46} The in-plane lattice constant of the heterostructure was fixed to that of Bi\textsubscript{3}Se\textsubscript{2}. DFT-D3 van der Waals corrections\textsuperscript{67} were applied for accurate structure optimization. The Chern number was calculated for a symmetric MnBi\textsubscript{3}Se\textsubscript{2}/SiQL-Bi\textsubscript{3}Se\textsubscript{2}/
MnBi₂Se₄ slab by using the method based on tracking the evolution of hybrid Wannier functions realized in Z2 Pack.⁸

■ ASSOCIATED CONTENT

Supporting Information
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Additional details on ARPES, SARPES, ab initio calculations, SQUID, and XMCD measurements (PDF)

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