The Layer-Inserting Growth of Antiferromagnetic Topological Insulator MnBi$_2$Te$_4$ Based on Symmetry and Its X-ray Photoelectron Spectroscopy

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Abstract

The antiferromagnetic topological insulator has attracted lots of attention recently, as its intrinsic magnetism and topological property make it a potential material to realize the quantum anomalous Hall effect at relative high temperature. Until now, only MnBi$_2$Te$_4$ is predicted and grown successfully. The other MB$_2$T$_4$-family materials (MB$_2$T$_4$: M = transition metal or rare earth element, B = Bi or Sb, T = Te, Se, or S) with not only antiferromagnetic topological property but also rich and exotic topological quantum states and dynamically stable (or metastable) structure have not been realized on experiment completely. Here, MnBi$_2$Te$_4$ single crystals have been grown successfully by us. It shows typical antiferromagnetic character with Neel temperature of 24.5 K and a spin-flop transition at $H \approx 35,000$ Oe, 1.8 K. In order to obtain the other members of MB$_2$T$_4$-family materials, it is necessary to understand the growth mode of MnBi$_2$Te$_4$. Its growth mode may be the layer-inserting growth mode based on symmetry, which is supported by our X-ray photoelectron spectroscopy (XPS) result, as the intrinsic chemical states of Mn and Te of MnBi$_2$Te$_4$ are the same with those of inserting material $\alpha$-MnTe. Understanding the growth mode of MnBi$_2$Te$_4$ can help us to grow the other members of MB$_2$T$_4$-family materials.

Keywords MnBi$_2$Te$_4$ · Antiferromagnetic topological insulator · XPS

1 Introduction

The milestone discoveries of integer quantum Hall effect (QHE) and fractional QHE made the QHE one of the most important fields in modern condensed matter physics. The dissipationless chiral edge states of the QHE regime can be used in low power consumption, high speed electronic devices. The unique chiral edge states responsible for the QHE originate from the magnetically induced Landau levels [1]. However, well-defined Landau levels are only possible in high-mobility samples under strong external magnetic fields. The demanding requirements prevent the QHE from being widely applied in industry. Therefore, it is highly desirable to achieve the QHE without the need of a strong magnetic field and an extraordinarily high-mobility sample. The anomalous Hall effect (AHE) in a ferromagnet can be induced by spontaneous magnetization without needing an external magnetic field [2]. Then, a quantized version of the AHE, the quantum anomalous Hall effect (QAHE), representing the realization of the QHE in the zero magnetic field has come to the forefront [2, 3]. When QAHE is realized, one can observe a plateau of Hall conductance ($\rho_{xy}$) of $e^2/h$ and a vanishing longitudinal conductance ($\rho_{xx}$) even at zero magnetic field (Fig. 1) [4]. Then, the realization of the QAHE may lead to the development of low-power-consumption electronics. There are two prerequisites for the
been realized in Fe- or Mn-doped Bi$_2$Se$_3$ [12, 13]. For Co- as Mn, Fe and Co into the TI. The opening of the gap has become a major research direction in the field of topological quantum materials.

Therefore, seeking new fundamental physics and technological applications based on this exotic phenomenon [11]. Therefore, seeking new materials to realize QAHE at higher temperature has become a major research direction in the field of topological quantum materials.

One approach is to try to dop the other 3d elements such as Mn, Fe and Co into the TI. The opening of the gap has been realized in Fe- or Mn-doped Bi$_2$Se$_3$ [12, 13]. For Co-doped TI, ferromagnetic behaviour and antiferromagnetic behaviour have been observed in Bi$_{1-x}$Co$_x$Se$_3$ [14, 15] and Sb$_{2-x}$Co$_x$Te$_3$ [16], respectively. Another approach is to use the magnetic proximity effects (MPEs) to induce magnetic order in a TI by coupling it to an adjacent magnetically ordered material. Lots of excellent works have been done such as the reports on EuS/TI [17–19], Y$_3$Fe$_5$O$_{12}$/TI [20–22], CrSb/TI [23],Tm$_3$Fe$_5$O$_{12}$/TI [24] and CrSe/TI [25]. Another promising approach is to realize high-temperature QAHE insulator in thin films of intrinsic ferromagnetic (FM) or antiferromagnetic (AFM) TI materials [26]. Nevertheless, despite much theoretical and experimental work were done to treat MnBi$_2$Te$_4$ as a kind of antiferromagnetic topological insulator [27–32]. On experiment, MnBi$_2$Te$_4$ could be synthesized through several approaches, but it is not so easy to get the high purity crystalline samples with perfect antiferromagnetic order [32, 35]. Then, to understand its growth mechanism becomes an urgent necessity. In another aspect, it is proposed that MnBi$_2$Te$_4$ is just one member of MB$_2$T$_4$-family materials (MB$_2$T$_4$: M = transition metal or rare earth element, B = Bi or Sb, T = Te, Se, or S) [28, 36, 37], which have rich topological quantum states. Among them, MnBi$_2$Te$_4$ has been grown successfully and tested, but the other materials of this family with dynamically stable structure have not been realized completely until now. Then, understanding the growth mechanism can help researcher to get the single crystals of the other family members too. Recently, Li et al. have reported the growth of high quality MnBi$_2$Te$_4$ with perfect antiferromagnetic order [32]. Based on the result of high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), they proposed the growth mechanism of MnBi$_2$Te$_4$ was the intercalation of MnTe into Bi$_2$Te$_3$ [38]. Be synchronous with their work, we have grown high quality MnBi$_2$Te$_4$ single crystal with perfect antiferromagnetic order too. Our experiences in the synthesis of layered iron-based superconductor ThFeAsN, ThCoAsN and ThMnAsN [39–41] with ThN layer as the block layer inspire us to consider that the growth mode of MnBi$_2$Te$_4$ may be the layer-inserting growth mode. To check it, the chemical states of MnBi$_2$Te$_4$ and $\alpha$-MnTe were investigated by XPS combing with the $Ar^+$ ion sputtering. After all, the measurement result supports our guess. Recently, there is new research progress in the intrinsic magnetic topological insulator and QAHE too. There are several reports on the van der Waals gap inserting growth of (MnBi$_2$Te$_4$)(Bi$_2$Te$_3$)$_m$, i.e. inserting Bi$_2$Te$_3$ to the van der Waals gap of MnBi$_2$Te$_4$ [42–45]. With the increasing of $m$, the interlayer antiferromagnetic exchange coupling of (MnBi$_2$Te$_4$)(Bi$_2$Te$_3$)$_m$ becomes gradually weakened, as the separation of magnetic layers increases. With $m = 3$, it shows long-range ferromagnetic order below 10.5 K, with the easy axis along the c axis [45]. At the same time, the zero-field QAHE has been realized in pure MnBi$_2$Te$_4$ at 1.4 K by Deng et. al., recently [46].

2 Experimental Section

2.1 Growth of MnBi$_2$Te$_4$ Single Crystals

Bi powder (99.99%), Te powder (99.999%) and Mn powder (99.9%) were all bought from Aladdin Company of China. $\alpha$-MnTe polycrystalline samples were prepared by mixing the powder components of Mn and Te in an atomic ratio
1:0.97. Then, the mixture was placed in an Al2O3 crucible and sealed in an evacuated quartz tube. The quartz tube was initially heated up to 700 °C at a rate of 2 °C/h, holding at this temperature for one day followed by water quenching. The growth process of Bi2Te3 is as following: Bi powder and Te powder were mixed according to the stoichiometric ratio. Then, the mixture was placed in an Al2O3 crucible and sealed in an evacuated quartz tube. The quartz tube was initially heated up to 850 °C in 5 h and then kept at this temperature for about 20 h. Next, the temperature was decreased to 550 °C in 48 h. After that, it was kept at 550 °C for 5 days then the heating program was closed. After that, the Bi2Te3 single crystal was gotten and then was smashed into powder to be utilized as precursor. High quality single crystals of MnBi2Te4 were synthesized using the flux method. The raw materials of α-MnTe and Bi2Te3 were mixed in the molar ratio of 1:5.85 in an Al2O3 crucible, which were sealed inside a quartz ampule. The ampule was put into a furnace and heated to 950 °C over a period of one day. After maintaining it at 950 °C for 12 h, the ampule was cooled to 580 °C at a rate of 10 °C/h. Large-sized MnBi2Te4 crystals were obtained after centrifuge in order to remove the excess Bi2Te3 flux.

2.2 Physical Properties Measurements

XPS were performed on Axis Ultra of Kratos Analytical with AlKα (hν = 1486.6 eV) as the monochromatic X-ray radiation source. The electron analyzer pass energy was fixed at 30 eV. The pressure in the spectrometer chamber was maintained at about 8×10−10 Pa. The binding energy (BE) scale was referenced to the energy of the C1s peak of adventitious carbon, E_B = 284.8 eV. All peaks had been fitted using a Shirley background and Voigt (mixed Lorentzian-Gaussian) line shapes. In order to remove the surface contamination and oxidation layer, then to observe the intrinsic chemical states of α-MnTe and MnBi2Te4, sputtering procedure was done by utilizing the Argon ion gun. For both bulk single crystal MnBi2Te4 and polycrystal α-MnTe, about 200-nm-thick film was removed within 180 s. For the argon ion gun, the estimated sputtering rate is about 1.1 nm/s and the ion energy is 1000 eV. The analysis software CasaXPS is used to fit the peaks. The magnetization measurements were performed in a Quantum Design superconducting quantum interference device vibrating sample magnetometer system (SQUID-VSM).

3 Results and Discussion

3.1 Crystal Structure and XRD Result

Bi2Te3 with rhombohedral crystal structure (trigonal phase) belongs to the space group of D3d (R̅3m), with five-atom layers arranging along the c-direction in one unit cell forming a Te-Bi-Te-Bi-Te quintuple layer. The coupling is strong between two atomic layers within one quintuple layer but much weaker, predominantly of the van der Waals type, between two quintuple layers [47]. Sharing the isostructure with Bi2Te3, MnBi2Te4 crystallizes in a rhombohedral layered structure belonging to R̅3m space group too. Similar with Bi2Te3, each layer of a unit cell has a triangular lattice with atoms ABC stacked along the c axis [26, 35]. Slightly differently, monolayer MnBi2Te4 includes seven atoms in a unit cell, forming a Te-Bi-Mn-Te-Bi-Te septuple layer (SL), which can be viewed as intercalating a Mn-Te bilayer into the center of a Bi2Te3 quintuple layer (QL) (Fig. 2).

As shown in the experimental section, the MnBi2Te4 is synthesized by self-flux method, through mixing α-MnTe and Bi2Te3 together, using Bi2Te3 as the flux agent. After being heated to 950 °C and held for one day, the mixture are cooled slowly to 580 °C. During the crystal growth process, the MnTe layers inserts into the Bi2Te3 layers and then MnBi2Te4 single crystal are gotten. Here, we can use some theories summarized for layered iron-based superconductors to help us to understand the layer-inserting growth of MnBi2Te4 [48]. It may follow such key points: I) The inserting layers (MnTe bilayer) and the inserted layers (Bi2Te3) share the similar crystal structure. Bi2Te3 with trigonal phase belongs to R̅3m(166) space group, while α-MnTe with hexagonal phase belongs to P63/mmc (194) space group, which is stable in bulk form. As shown by Fig. 2, both unit cells of α-MnTe and Bi2Te3 have layered structure, with the trigonal layer and hexagonal layer alternately stacking along the c axis, which makes the insertion of α-MnTe possible. However, it is predicted that rhombohedral MnBi2Se4 (R̅3m(166) space group) is also a kind of antiferromagnetic topological insulator [36]. We have tried several times to get the bulk rhombohedral structure MnBi2Se4 by the similar inserting method, but it is not successful. What we have done is that, we use α-MnSe of NaCl structure (Fm3m space group of cubic system and the stable phase of manganese selenium compounds) as the inserting layer material to try to insert it into the rhombohedral Bi2Se3. Then, it can be explained from the symmetry perspective: inserting α-MnSe with NaCl structure into rhombohedral (trigonal phase) Bi2Se3, just like inserting a square into a stack of triangle (or regular hexagon), which is not permitted by the symmetry and not stable too. We think the symmetry is the major obstacle to hinder the formation of rhombohedral MnBi2Se4 which is a potential antiferromagnetic topological insulator. II) Lattice mismatch between α-MnTe and Bi2Te3 is acceptable. According to the powder XRD pattern shown by Fig. 3, we have refined lattice parameters of α-MnTe which are a = 4.1477 Å, c = 6.7123 Å, while for that of Bi2Te3 are a = 4.384 Å, c = 30.488 Å, respectively. As the lattice
parameters mainly influencing the inserting process is from a axis, the lattice mismatch between $\alpha$-MnTe and Bi$_2$Te$_3$ in a axis is calculated, which is only 3.4% ($\frac{a_{\alpha} - a_0}{a_0} \times 100\%$).

III) Self-stability of $\alpha$-MnTe. The bulk $\alpha$-phase of MnTe is stable at room temperature and atmospheric pressure. IV) There exists charges transfer between the inserting layers (MnTe) and the inserted layers (Bi$_2$Te$_3$). As shown by Fig. 2c, d and e that, during the inserting growth process bilayer -Mn-Te- of $\alpha$-MnTe would insert into the gap between the third layer (Te atoms layer) and fourth layer (Bi atoms layer) of the unit quintuple layer of Bi$_2$Te$_3$. Therefore, Mn atoms of $\alpha$-MnTe would bond with Te atoms of Bi$_2$Te$_3$, then Mn atoms would transfer electrons to Te; Te atoms of $\alpha$-MnTe would bond with Bi atoms of Bi$_2$Te$_3$, then Bi atoms would transfer electrons to Te. The charges transfer can make the MnBi$_2$Te$_4$ system stable. In summary, the growth mode of MnBi$_2$Te$_4$ has typical character of inserting layer mode.

3.2 Magnetic and Transport Properties

Figure 4a shows the temperature-dependent magnetic susceptibility of MnBi$_2$Te$_4$ single crystal measured at 10,000 Oe. It could be observed that MnBi$_2$Te$_4$ shows antiferromagnetic behaviour with $T_N = 24.5$ K. Meanwhile, a strongly anisotropic magnetic susceptibility is observed.

![Fig. 2](image)

*Fig. 2.* The illustration of layer-inserting growth process of MnBi$_2$Te$_4$. MnBi$_2$Te$_4$ includes seven atoms in a unit cell, forming a Te-Bi-Te-Mn-Te-Bi-Te septuple layer (SL). The inserted part of the figure is the single crystal of MnBi$_2$Te$_4$. It is about $3 \times 1.5$ mm$^2$ in dimension.

![Fig. 3](image)

*Fig. 3.* a and b are the powder XRD pattern of $\alpha$-MnTe and Bi$_2$Te$_3$, respectively. The inserted part of a and b are the crystal morphology of $\alpha$-phase MnTe polycrystals and Bi$_2$Te$_3$ single crystal, respectively.
The magnetic susceptibility of \( \chi \) of MnBi\(_2\)Te\(_4\) as a function of temperature measured in an external magnetic field of \( H = 10,000 \) Oe in zero-field-cooled (zfc) mode. The right axis of ordinates shows the temperature-dependent reciprocal susceptibility of \( H//c \). The pink line is a fitted line according to modified Curie-Weiss law, fitted in the range of 30 K to 300 K (\( \chi_0 = 0.0029 \) emu/mol Oe).

Field-dependent magnetization curves for two directions measured at 1.8 K and 300 K. The magnetic susceptibility of \( H//c \) displays much steeper transition below 24.5 K, which means the c axis is the easy axis. A modified Curie-Weiss law \( \chi(T) = \chi_0 + C/(T-\theta_{cw}) \) is used to fit the paramagnetic regime above \( T_N \) in the range of 30 K to 300 K. Here, \( \chi_0 \) means a temperature-independent magnetic susceptibility, which contains two parts: one is diamagnetism closed electron shells; the other one is the Pauli paramagnetism due to the metallicity of MnBi\(_2\)Te\(_4\). The temperature-dependent Curie-Weiss susceptibility \( C/(T-\theta_{cw}) \) is mainly from localized Mn moments. The fitted effective paramagnetic moment with the value of 5.0\( \mu_B \) roughly agrees with the high-spin configuration of Mn\(^{2+} \) (\( S = 5/2 \)) [29]. Meanwhile, the Curie-Weiss temperature \( \theta_{cw} = 3.1 \) K strongly depends on the fitted \( \chi_0 \) contribution. Below \( T_N \), a spin-flop transition at \( H \approx 35,000 \) Oe is observed for \( H//c \) (Fig. 4b) in the M-H curve, which is in line with the M-T result suggesting that c axis is the easy axis. To check its magnetic properties further, field dependence of magnetization of MnBi\(_2\)Te\(_4\) single crystal has been measured at different temperatures under the magnetic field of \( H//c \) and \( H\perp c \). Its temperature dependence of magnetic susceptibility has been measured under magnetic field too (see Fig. S1 of the Supplementary Materials). As shown by Fig. S1a that, for \( H//c \), above \( T_N \), the magnetization displays a linear dependence, indicating the paramagnetic state; below \( T_N \), all the curves show spin-flop transition. Figure S1c and d show the temperature dependence of the magnetic susceptibility measured in various magnetic fields applied parallel and perpendicular to the crystallographic c axis, respectively. With increasing magnetic fields, the magnetic order is suppressed to lower temperatures, which agrees with previous reports [30, 32]. The magnetic measurement result shows that the MnBi\(_2\)Te\(_4\) single crystal owns good crystal quality and well antiferromagnetic property. As shown by Fig. 5, complementarily to the magnetic measurements, the temperature dependence of the in-plane electrical resistance R(T) of a bulk MnBi\(_2\)Te\(_4\) single crystal was measured from room temperature down to \( T = 2.0 \) K. The resistance decreases with lowering the temperature, which is the metallic behaviour. The R-T curve exhibits a distinct peak-like feature centered at 24.0 K. Around the peak, the local increase indicates an enhanced electron scattering in the vicinity of a magnetic phase transition, and a sharp decrease below the peak signals the freezing-out of the scattering due to an onset of long-range magnetic order, respectively [31, 49]. This is consistent with the magnetic measurement result.

### 3.3 XPS Result

The sputtering procedure is done to remove the surface contaminants of MnBi\(_2\)Te\(_4\) (001). As illustrated by Fig. 6, compared to the initial spectrum (above line), the spectrum obtained from the cleaned surface (below line) does not show surface contaminants, i.e. oxygen and carbon anymore.

Figure 7 shows the XPS spectrum of Mn2p, Te3d and Bi4f. Their fitted parameters are shown in Table 1. Deconvolution of the Mn2p spectrum of Fig. 7a reveals two main contributions: Peak 1 at the position of 640.8 eV and Peak 2 with \( E_B = 642.1 \) eV. Compared with the reference data [50], it is found that Peak 2 corresponds to Mn-O bond of MnO\(_2\). Considering the overlap of the binding energy of MnO and MnTe [51], Peak 1 of Fig. 7a may be a sum of two partial contributions: MnO and MnTe. However, it is difficult to separate Peak 1 into two reasonable parts. Peak...
3 shifting to higher energies can be ascribed to the satellite of Peak 1 [51–55]. The satellites are also called shakeup satellites. It locates at the higher-binding-energy side of the relevant core-lines of transition metal (TM) or rare earth (RE) ions in the selected TM or RE compounds [56]. It also concerns on particular binary Mn oxides, especially MnO [55]. Such satellite structure in Mn 2p XPS spectrum originates from charge transfer between outer electron shell of ligand and an unfilled 3d shell of Mn during creation of core-hole in the photoelectron process [53–55]. For Fig. 7c, Peak 1 at the position of 639.8 eV corresponds to +1 charge state of Mn, which may come from nanoclusters of manganese subtelluride (possibly Mn2Te), created in the surface and subsurface region penetrated by Ar+ ions [34]. Peaks 3 is the corresponding satellite of Peak 1. In addition, rising intensity of the Mn2p satellite for divalent Mn (bound to chalcogen) with atomic number of ligand (from MnO to MnBi2Te4) could be observed too. As shown by Fig. 7e and f that the peaks’ positions of Te3d of α-MnTe almost overlap with those of MnBi2Te4, which means that the chemical states of Te both from α-MnTe and MnBi2Te4 are the same. Figure 7g and h are the XPS spectra of Bi4f acquired from the MnBi2Te4 surface without and with sputtering, respectively. As shown by Fig. 7g that peak 1 locating at the position of 157.3 eV corresponds to Bi-Te bond, while peak 2 locating at the position of 158.8 eV corresponds to Bi-O bond of Bi2O3 [58, 59]. As shown by Fig. 7h that, after the sputtering is done, there exists only one kind of bond i.e. Bi-Te bond with the binding energy of 157.4 eV. This tells us again that the contaminants have been removed completely by the sputtering procedure. Comparison of the fitted Mn2p and Te3d parameters of the MnBi2Te4 and α-MnTe spectral components gathered in Table 1, it shows a very good consistency between them (considering the accuracy of the method, i.e. ΔE = 0.1 eV). Then, we can get the conclusion that, Mn and Te of MnBi2Te4 share the same chemical state with those of α-MnTe, which supports our hypothesis that the growth mode of MnBi2Te4 is the inserting-layer growth mode.

4 Conclusion

Single crystals of antiferromagnetic topological insulator MnBi2Te4 have been grown by flux method. The magnetic property of MnBi2Te4 is investigated, which shows good antiferromagnetic character with Neel temperature of 24.5 K and a spin-flop transition at H ≈ 35,000 Oe, 1.8 K. The possible inserting-layer growth mode of MnBi2Te4 is proposed, which is supported by the XPS and XRD.
Fig. 7  a and b are the XPS spectra of Mn2p core-level acquired from α-MnTe, without and with sputtering, respectively. c and d are the XPS spectra of Mn2p core-level acquired from the MnBi2Te4 surface without and with sputtering, respectively. e and f are the XPS spectra of Te3d obtained from sputtered α-MnTe and MnBi2Te4, respectively. g and h are the XPS spectra of Bi4f core-level acquired from the MnBi2Te4 surface without and with sputtering, respectively. For all the panels, the peaks are numbered increasingly from right to left as Peak 1 (P1), Peak 2 (P2), Peak 3 (P3), … . Meanwhile, RD denotes the raw data; BL means the base line; FT corresponds to the fitted line result of α-MnTe and MnBi2Te4. The proposed crystal growth mechanism may help us to grow the other members of MB2Te4-family materials, which have rich topological quantum states. The XPS measurement combing with the Ar⁺ ion sputtering is done to investigate chemical states of MnBi2Te4 and α-MnTe. Binding energies of MnBi2Te4-related contributions to the Mn2p and Te3d spectra agree well with those of α-MnTe.
Table 1 The fitted peaks’ position of Mn2p and Te3d of α-MnTe and MnBi2Te4, respectively. S, sputtering; WTS, without sputtering

| Table 1 |  |
| --- | --- |
| Mn2P3/2 | MnTe | WTS | S | D40.8 | MnO and MnTe |
| S | P1 | 639.8 | Mn subteluride |
| WTS | P2 | 642.1 | MnO2 |
| S | P2 | 641.1 | MnTe |
| WTS | P3 | 646.1 | Satellite of P1 |
| S | P3 | 643.5 | Satellite of P1 |
| WTS | P4 | 646.3 | Satellite of P2 |

| MnBi2Te4 | WTS | P1 | 640.6 | MnO and MnTe |
| S | P1 | 639.8 | Mn subteluride |
| WTS | P2 | 642.1 | MnO2 |
| S | P2 | 641.1 | MnTe |
| WTS | P3 | 644.2 | Satellite of P1 |
| S | P3 | 643.9 | Satellite of P1 |
| WTS | P4 | 647.4 | Satellite of P2 |
| S | P4 | 646.4 | Satellite of P2 |

| Te3d5/2 | MnTe | S | 571.9 | Mn-Te |
| MnBi2Te4 | S | 572.0 | Mn-Te |

| Bi4f7/2 | MnBi2Te4 | WTS | P1 | 157.3 | Bi-Te |
| S | 157.4 | Bi-Te |

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