

**Bi$_{11}$Te$_1$: a dual topological insulator**

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A combined theoretical and experimental study reveals evidence for the dual topological insulating character of the stoichiometric natural superlattice phase Bi$_{11}$Te$_1$ = [Bi$_2$]$_1$[Bi$_2$Te$_3$]$_2$, being a stack of alternating Bi bilayers and two quintuple layers of Bi$_2$Te$_3$. We identify Bi$_{11}$Te$_1$ by density functional theory to exhibit a non trivial time-reversal symmetry-driven character of Z$_2$ = (0; 001) and additionally a mirror-symmetry induced mirror Chern number of n$_M$ = –2, which indicates that Bi$_{11}$Te$_1$ is both a weak topological insulator and a topological crystalline insulator. The coexistence of the two phenomena preordains distinct crystal planes to host topological surface states that are protected by the respective symmetries. The surface perpendicular to the stacking direction is the ‘dark’ surface of the weak topological insulator, while hosting mirror-symmetry protected surface states along the TFI direction at non-time-reversal invariant momenta points. We confirm the stacking sequence of our MBE-grown Bi$_{11}$Te$_1$ thin films by X-ray diffraction and transmission electron microscopy, and find indications of the topological crystalline and weak topological character in the surface electronic spin structure by spin- and angle-resolved photoemission spectroscopy, which nicely match the results from density functional theory.

**INTRODUCTION**

Topological insulators (TIs) are bulk insulating materials which exhibit perfect metallic conductivity on their boundary via electronic edge (in 2D TIs) or surface states (in 3D TIs) that are guaranteed by the topological character of the bulk band structure [1–2]. Electrons in these boundary states are highly spin-polarized and their spin and momentum is locked to each other by spin-orbit coupling, creating helical spin textures and making TIs highly attractive for spintronic applications [3]. One of the most exciting aspects of 3D TIs is the fact that their surface inevitably hosts these metallic surface states as long as the symmetry defining the topological character is not destroyed [4–5]. In a strong topological insulator (STI), for instance, time-reversal symmetry protects these states on all surfaces. Weak topological insulators (WTIs), on the other hand, display protected metallicity only at surfaces with a certain orientation, while other surfaces remain insulating. The latter can be understood in a simple picture, where a stack of two-dimensional TIs forms a WTI with metallic edge states inherited from the 2D TI but with an insulating surface plane (the ‘dark side’) normal to the stacking direction. Finally, in topological crystalline insulators (TCIs), where the symmetry with respect to a mirror plane defines the topology, the metallic surface states can be found on surfaces perpendicular to these mirror planes [6–7].

For the case of Bi$_2$Te$_3$ it was already shown that a single compound can belong both to the class of strong TIs and TCIs [8]. It is intriguing to think of the possibilities opened by symmetry breaking that can destroy certain surface states while keeping others intact. For example one could imagine a material that is both a WTI and a TCI and has all surfaces covered with metallic edge states, where the mirror plane of the TCI is normal to the dark side of the WTI. Then, a magnetic field would destroy the topological protection of the states originating from the topological properties that define the WTI, while the mirror-symmetry protected states remain intact: Likewise, small structural distortions can destroy the mirror plane without affecting the edge states arising from time-reversal symmetry. In the search for such a material, we start from Bi$_2$Te$_3$ with the above mentioned properties and from the Bi bilayer that is known to be a 2D TI [9–11]. It is possible to produce natural superlattices [Bi$_2$]$_x$[Bi$_2$Te$_3$]$_y$ from hexagonal, metallic Bi bilayer (BLs) and semiconducting Bi$_2$Te$_3$ quintuple layer (QLs) building blocks in a wide range of x and y [12–15]. While Bi$_2$Te$_3$ consists of only QL building blocks, the unit cell of Bi$_{11}$Te$_1$ phase is made out of a stacking sequence of a single BL interleaved with two subsequent QLs. The size of the unit cell along the stacking direction, i.e. the c lattice constant, varies quite severely among the different stable compounds, which makes them easily distinguishable in a diffraction
experiment. Recently, Bi$_2$Se$_3$ (i.e. $x = y = 1$) was investigated in some detail and characterized as topological semimetal [15]. For practical applications, however, an insulating bulk material is preferable.

In this article, we identify the stoichiometric natural superlattice Bi$_1$Te$_1$ (i.e. $x = 1, y = 2$) as a semiconductor with a small bandgap of about 0.1eV with the desired properties: Bi$_1$Te$_1$ is both a WTI and a TCI where the combination of both properties leads to topologically protected surface states (TSS) on all sides of the crystal. Our density functional theory (DFT) calculations predict a $Z_2$ class of (0;001) and a mirror Chern number $n_M = -2$. We find two characteristic surface states of the TCI on the (0001) surface, regardless of the surface termination. A very similar situation has been reported recently for Bi$_2$TeI, theoretically [17].

We demonstrate that Bi$_1$Te$_1$ can be grown in form of high quality thin films on Si(111) by molecular beam epitaxy (MBE). Its layered structure is confirmed by scanning transmission electron microscopy (STEM) and X-ray diffraction (XRD), confirming a repeated stacking sequence of 2QL of Bi$_2$Te$_3$ and a single Bi BL. We investigate the electronic structure of Bi$_1$Te$_1$ by means of spin- and angle-resolved photoemission (spin-ARPES). The experimental results are compared to the well known prototypical 3D STI Bi$_2$Te$_3$ ($x = 0, y = 3$). Spin-ARPES reveals that in Bi$_1$Te$_1$ the surface states close to $E_F$ exhibit a nearly vanishing spin polarization in contrast to the time-reversal symmetry driven TSS in Bi$_2$Te$_3$. Furthermore, our spectra taken along non-high-symmetry lines reveal band crossings at non-time-reversal invariant momenta (TRIM) points that can be associated with surface states protected by mirror symmetry and the TCI character of Bi$_1$Te$_1$.

**RESULTS & DISCUSSION**

**Ab-initio calculations.**

Figure 1(a) depicts a schematic model of the crystal structure of Bi$_1$Te$_1$, indicating Te (green) and Bi (orange) atoms as well as one unit cell defined by the lattice constant $c$ along the stacking direction. The separation of the layered structure into QLs and Bi BLs is marked. The bulk band structure of Bi$_1$Te$_1$ in the relaxed structural geometry is presented in Fig. 1(b). Spin-orbit coupling is included in this calculation and the color represents the localization of the electronic states at the BL (green) or at the QL (red). As one can see, there are no states at the Fermi level $E_F$, reflecting the insulating character with an energy gap of 73 meV. The states around the Fermi level alternate between BL- and QL-related, where the highest occupied levels at the time-reversal invariant momenta $\Gamma$ and $A$ stem from QLs (red), while the lowest unoccupied states originate from the BL (green), and vice versa for the $M$ and $L$ points. Since the crystal possesses spatial inversion symmetry, the parity of the states can be calculated and the topological index $Z_2$ can be deduced according to ref. [15] based on the product of the parities of all occupied bands at the eight TRIMs, i.e., one at $\Gamma$, one at $A$, three at $M$, and three at $L$. The result is shown in Fig. 1(c) for the corresponding TRIMs, $\Gamma$ and $A$ have parity products of +1 (red ‘+’) while $M$ and $L$ have −1 (blue ‘−’), leading to a topological invariant $Z_2 = (0;001)$. Therefore, Bi$_1$Te$_1$ is a weak topological insulator with the (0001) surface, which is perpendicular to the stacking direction, being the “dark” surface and being free of time-reversal symmetry protected surface states.

It is tempting to relate the WTI property to the fact that both, the Bi bilayer and the 2QLs Bi$_2$Te$_3$ are 2D TIs such that the WTI results from a simple stacking of 2D TIs in the c-direction. However, our band structure calculations in Fig. 1(d), introducing artificially expanded distances between the BL and the QLs, show a more complex scenario: If the BL is sufficiently separated from the 2QLs, the states can be decomposed in contributions from the two components (green = Bi BL and red = 2QLs, respectively). But, due to charge transfer, the inverted gap of the BL is shifted above the Fermi level and, accordingly, some of the 2QL Bi$_2$Te$_3$ conduction band states are below $E_F$. Only the hybridization of the BL states with the QL states opens up the gap that leads to the insulating bulk structure in Fig. 1(d), as can be nicely deduced from the changing color of the bands along the $k$-directions. Nevertheless, the topological character of the stacked film remains non-trivial. A similar complexity is also found for the first confirmed, stacked weak TI Bi$_{14}$Rh$_9$I$_9$ [19–21].

Next, we want to examine the surface bandstructure on the (0001) surface, which heavily depends on the precise surface termination. Due to the layered crystal structure and the weak van der Waals bonds between the subsequent building blocks, there exist three natural cleavage planes and thus surface terminations, i.e., 1Bi BL, 1QL, and 2QL. Figure 2 depicts the spin-resolved surface bandstructure for the respective terminations. In all cases an even number of Fermi level crossings is found in $\Gamma\bar{M}$ direction, while along $\Gamma\bar{K}$ a bandgap between valence- and conduction band is formed (although it can be very small). We see that, although there are surface states, the bandstructure is formed with a WTI phase. Nevertheless, it is remarkable that the bands along $\Gamma\bar{M}$ show a band crossing for all possible terminations, reminiscent of Dirac-like cones observed in topological crystalline insulators. Additional evidence that this crossing is protected by a mirror symmetry in
FIG. 1. Bulk band structures of Bi$_3$Te$_1$. (a) Simple sketch of the crystal structure of Bi$_3$Te$_1$. The unit cell consists of 1 Bi BL and 2 QLs. (b) and (d) show the bulk band structure calculation in the structurally relaxed geometry and with artificially expanded distances between the BL and the QLs, respectively. States localized mostly in the BL are marked in green, while the states localized mostly in the QLs are shown in red. In (b), the band structure of the BL shows an inverted gap about 0.2 eV above the Fermi level ($E_F$ marked with a dashed line). (c) Bulk and surface Brillouin zone with parity product of the TRIM points resulting in +1 (red ‘+’) or -1 (blue ‘-’). $k_z$ direction corresponds to the stacking direction. ΓAML, i.e. ($k_x, k_z$)-plane, marks a mirror plane.

FIG. 2. Spin-resolved DFT surface electronic structure calculations along MΓM of slabs of Bi$_3$Te$_1$ terminated by a Bi BL (left), a single QL (center), and two QLs (right) with bulk projected bands in gray and surface bands in colors. The size of the symbols corresponds to the spin-polarization in the first four layers of a slab, the color (red/blue) indicates the orientation of the spins with respect to a direction perpendicular to the momentum and surface normal.

the crystal comes from the observation that the crossing is lifted when the surface atoms are displaced in [11$ar{2}$0] direction, breaking this symmetry (not shown here).

To check for the possibility that Bi$_3$Te$_1$ is a TCI, we determined the mirror Chern number of the bulk phase. In the ($k_x, k_z$) plane in reciprocal space (Fig. 1(c)) all Bloch states can be distinguished by their eigenvalues with respect to a mirror operation in the (1T00) plane. To calculate their corresponding Berry phases as well as the Chern numbers, we construct a tight-binding Hamiltonian based on the maximally localized Wannier functions. The Chern numbers of all occupied bands for the opposite mirror eigenvalues $+i$ and $-i$ are $n_{+i} = 2$ and $n_{-i} = -2$, respectively, and therefore the mirror Chern number $n_M$ is $n_M = (n_{-i} - n_{+i})/2$, is $n_M = -2$, confirming the fact that Bi$_3$Te$_1$ is a TCI.

Lets discuss the individual features of the different terminations shown in Fig. 2 in more detail. The BL terminated surface is characterized by surface states that disperse from the $\Gamma$ point at $-0.2$ eV downwards, very similar to features observed for a single Bi bilayer on Bi$_2$Te$_3$ [22, 23]. The steeply dispersing bands near $\Gamma$, crossing at $0.3$ eV, are a characteristic feature that is also observed for a Bi-rich termination of Bi$_4$Se$_3$ [24]. In contrast, the QL-terminated surface (center panel of Fig. 2) shows near the Fermi level only the linear crossing of bands that is protected by mirror symmetry. Strongly spin-polarized surface states are observed around 1.0 eV, which are similar to the states that also characterize the surface of Bi$_2$Te$_3$ [25] or Sb$_2$Te$_3$ [26]. These Rashba-split surface states equally appear on the 2QL terminated surface (right in Fig. 2). In this case more states appear near the Fermi level (although leading to an even number of crossings, compatible with the weak topological character).
Crystallographic structure. Surface electronic structure by ARPES.

The comparative results of our ARPES investigations on vacuum transferred, as-grown Bi$_2$Te$_3$ and Bi$_3$Te$_1$ thin films is summarized in Fig. 4. As mentioned and confirmed above, we consider the as-grown Bi$_3$Te$_1$ surface as Bi-poor. In the case of the prototypical STI Bi$_2$Te$_3$ our results nicely reproduce earlier findings [25].

In general, the spectra exhibit sharp features and a very good signal to noise ratio revealing the high crystalline quality of the thin films. This is also reflected in the low-energy electron diffraction pattern in Fig. 4(a) and (e), where the orientation of the surface Brillouin zones is illustrated. Figure 4(b) and (f) depict wide range binding energy $E_B$ vs. wavevector $k_{||,x}$ maps of Bi$_2$Te$_3$ and Bi$_3$Te$_1$, respectively, along trajectories in the $\Gamma K$ direction which traverse the $\Gamma$ point of the surface BZ recorded with $h\nu = 21.2$ eV. Already on first glance the spectra of the two samples show a lot of similarities but also some major differences (e.g. marked by the black arrows). Both samples are of n-type nature with the conduction band minimum (CBM) being cut by the Fermi level, but in Bi$_3$Te$_1$ there seems to be an even stronger considerable downshift of the entire valence band, due to a possible electron donation of the Bi bilayers to the QLs [16]. The downshift as well as the spectral changes are clearly revealed by the energy distribution curves (EDCs) in (i), which are obtained along normal emission, i.e., $k_{||,x} = 0 \text{ Å}^{-1}$ (left) and $k_{||,x} = 0.39 \text{ Å}^{-1}$ (right), marked by the dashed area in (b) and (f). Here, black arrows mark the spectral changes that can be attributed to additional features appearing in (f).

Additionally, in the wide range ARPES maps the spin-polarized surface electronic structure slab-calculations are superimposed (for 1QL surface termination in the case of Bi$_3$Te$_1$). Here, red and blue dots mark oppositely oriented in-plane spin channels and the size of the dots corresponds to the spin-polarization. The Fermi level in the calculation needed to be shifted upwards by 250 meV [100 meV] to fit better to the experimental data of Bi$_2$Te$_3$ [Bi$_3$Te$_1$]. The prominent and intense Rashba-type surface state located between $E_B = 0.7 - 1.05$ eV [0.95 - 1.3 eV] has been used as a gauge to match the calculation to the ARPES data. As one can see, the agreement between the data and DFT simulation is very high and most of the features can be matched. Only the predicted gap-opening along $\Gamma K$ in the uppermost prominent band, which we labeled $\beta$, is not reproduced in the experimental spectrum.

The reason why we do not resolve a gap-opening in the ARPES data, neither along $\Gamma\Xi$ nor $\Gamma K$ direction, is again most probably due to the lack of lateral resolution of our measurement technique. The vast variety of surface bands originating from different terminated...
FIG. 3. Bulk characterization of Bi$_1$Te$_1$ thin films. (a) Comparative XRD $\omega/2\theta$ scans for both Bi$_2$Te$_3$ and Bi$_1$Te$_1$ films averaged over the entire crystal with the derived $a$ and $c$ lattice constants, as highlighted. (b) Local STEM image of a 39 nm thick Bi$_1$Te$_1$ film confirming the high bulk crystalline quality. The contrast in the image scales with the atomic number squared ($Z^2$), i.e., bright = Bi, darker = Te. QLs and Bi BLs separated by van der Waals gaps can be identified. The yellow frame marks the region over which the line profile below is measured while averaging in vertical direction. QLs and BLs are denoted and Bi and Te atoms are displayed by orange and green columns, respectively.

FIG. 4. Comparative ARPES investigation on thin films of Bi$_2$Te$_3$ and Bi$_1$Te$_1$ at low temperatures $T \approx 25$ K. (a) [e] Low-energy electron diffraction pattern of a 19 nm Bi$_2$Te$_3$ [45 nm Bi$_1$Te$_1$] film for identification of the orientation of the surface Brillouin zone. (b) [f] Wide energy range $E_B$ vs. $k_{||,x}$ spectra along $\Gamma K$ direction of both samples measured with $h\nu = 21.2$ eV with superimposed spin-polarized DFT calculations from Fig. 2 (red and blue dots are opposite in-plane spin channels; 1QL termination is used for Bi$_1$Te$_1$). Black arrows in (f) mark prominent changes compared to (b). Dashed lines mark cuts of the energy distribution curves (EDCs) shown in (i). (c) [g] Magnified electronic structure close to the Fermi level for two different photon energies $h\nu = 21.2$ eV and 8.4 eV along indicated crystallographic directions. Conduction band minimum (CBM), Dirac point (DP) and topological surface state (TSS) marked by arrows. (d) [h] Plot of the inverse energy dispersion $k(E_B)$ of the right branch of the prominent TSS [$\beta$ state] for both photon energies as determined by Voigt fits to the momentum distribution curves in (c) [g]. (i) EDCs obtained from the spectra shown in (b) (black curve) and (f) (green curve) along $k_{||,x} = 0$ Å$^{-1}$ (left) and 0.39 Å$^{-1}$ (right). Black arrows mark spectral changes corresponding to the arrows in (f).
areas on the sample may easily provide states that overlap or even hybridize and thus close the gap. The right panel in Fig. 2 shows that the 2QL terminated surface provides states that close the gap also along \( \Gamma K \) direction. Section III in the supplementary material shows how the superposition of the calculated spectra for both 1QL and 2QL terminated surfaces hinders the observation of the band gap.

Panels (c) and (g) of Fig. 4 depict magnified close-Fermi level spectra of the \( h\nu = 21.2 \text{ eV} \) excitation along both \( \Gamma M \) and \( \Gamma K \) direction and the same spectra obtained using \( h\nu = 8.4 \text{ eV} \) along \( \Gamma K \). The two different photon energies are used to probe a different cut in the Fermi level spectra of the TSS and thus provide additional evidence of the surface state character of the states. Indeed, for Bi\(_2\)Te\(_3\) the TSS, driven by time-reversal symmetry, is well-known in literature, is revealed and the Dirac point (DP) is located around \( E_B \approx 300 \text{ meV} \) and buried in bulk valence band pockets.

On the other hand, the prominent and interesting \( \beta \) feature in Bi\(_1\)Te\(_1\) seems to disperse strongly linearly and could, on the first glance, be confused with a topologically non-trivial Dirac cone state. Indeed, the lack of \( k_\perp \)-dispersion of the TSS in Bi\(_2\)Te\(_3\) and the \( \beta \) band in Bi\(_1\)Te\(_1\) is quantified in Fig. 3(d) and (h), where the wave vector \( k_\parallel \) of the right branch of the TSS and the \( \beta \) state is plotted against the binding energy for the two different photon energies. The data points were extracted out of Voigt peak fits to the momentum distribution curves of both spectra in Fig. 4(c) and (g).

For the first 200 meV below \( E_F \), the fit is very good, i.e., the error very small, but the situation declines when the states start to hybridize with other bands at higher energies. The fact that the dispersion of those states is exactly the same for both 21.2 eV and 8.4 eV is a strong indication of their surface state character. Moreover, from this the Fermi velocity \( v_F \) can be determined by a linear fits as \( v_F = \frac{E}{k_F} \) to be \( v_F \approx 2.4 \text{ eVÅ} = 3.6 \cdot 10^5 \text{ m/s} \) for Bi\(_1\)Te\(_1\) and \( v_F \approx 3.2 \text{ eVÅ} = 4.8 \cdot 10^5 \text{ m/s} \) for Bi\(_2\)Te\(_3\).

A strong experimental evidence of the topological nature of a state is the verification of its helical spin polarization [2]. Thus, Fig. 5 summarizes our findings on the spin polarization of the \( \beta \) state of 'sputtered', i.e., Bi-rich, Bi\(_1\)Te\(_1\) (a)-(c). Again the data from Bi\(_1\)Te\(_1\) is compared to measurements on Bi\(_2\)Te\(_3\) and the spin polarization of the prototypical TSS (d)-(f).

Figure 5(a) and (d) again show the wide range ARPS maps of Bi\(_1\)Te\(_1\) and Bi\(_2\)Te\(_3\) from in Fig. 3(b) [f], respectively, which illustrate along which opposing \( k \)-points, marked by the red dashed area, the spin polarization is measured. Figures 5(b) and (c) as well as (e) and (f) depict the wide range and close-Fermi level (in-plane) spin-resolved partial intensities \( I_{\text{eff}} \) and \( I_{\text{right}} \) along the indicated \( k \)-points. The spectra were corrected by the asymmetry function of \( S = 0.27 \), and the net spin polarization is shown underneath.

Both samples show quite similar and rather high in-plane spin polarization of 40-50% in the bands at higher binding energies, around \( E_B \approx 3.2 \text{ eV} \), \( E_B \approx 2.1 \text{ eV} \) and \( E_B \approx 0.9 - 1.4 \text{ eV} \) in panels (b) and (e). The full reversal of the spin polarization between the two opposing \( k \)-points confirms the helical nature of these states in both samples. Further, the TSS of Bi\(_2\)Te\(_3\) shows a helical spin polarization of up to 40% in panel (f), which nicely confirms its topological nature and is in agreement with what was reported earlier [24]. On the contrary, panel (c) reveals that the most interesting \( \beta \) state in Bi\(_1\)Te\(_1\) at the Fermi level is measured to exhibit only very little (though non-vanishing) in-plane spin polarization of max. 10% and without a clear reversal at the opposing \( k \)-points. Such weak spin polarization can be induced by SOC in topologically trivial surface states, as most of the states in the calculated band structures in Fig. 2 already showed some non-zero spin polarization. Therefore, this measurement reveals a difference to the prototypical TSS and thus gives an experimental indication but no final proof about the topological character of the \( \beta \) state.

Finally, we are searching for an experimental evidence...
of the above mentioned mirror-symmetry protected band crossings at non-TRIM points, which are a consequence of the topological crystalline character of Bi$_1$Te$_1$. Therefore, Fig. 6 depicts experimental and calculated spectra along non-high symmetry lines which reveal a region in $k$-space, where the TCI-induced states can be identified and no other states interfere. Figure 6(a) shows a constant energy contour, i.e., $k_{||,x}$ vs. $k_{||,y}$ map, at $E_{\text{B}} = E_{\text{F}}$ with red dashed lines marking spectra taken along different cut directions at $k_{||,y} = 0.087$ Å$^{-1}$ (b), 0.120 Å$^{-1}$ (c), 0.152 Å$^{-1}$ (d), 0.184 Å$^{-1}$ (e), 0.216 Å$^{-1}$ (f), and 0.258 Å$^{-1}$ (g). The panels (b)-(g) depict the respective ARPES spectra obtained with 8.4 eV (top) as well as spin-polarized surface electronic structure calculations (bottom), which are performed for the 1QL terminated surface. Besides some additional features from different terminations in the experimental spectra at higher binding energies, the agreement is very good and one can clearly identify the interesting bands, which exhibit a mirror-symmetry protected crossing point around $k_{||,y} = 0.184$ Å$^{-1}$. We attribute these crossing bands at a non-TRIM point to be the consequence of the TCI character of Bi$_1$Te$_1$ and to be independent of the surface termination.

**SUMMARY AND CONCLUSIONS**

In summary, we predicted and demonstrated the dual topological insulator character of the stoichiometric natural superlattice phase Bi$_1$Te$_1$ by a combined theoretical and experimental investigation. Our study theoretically predicts by ab initio DFT calculations that Bi$_1$Te$_1$ exhibits a 'dark' surface perpendicular to the stacking direction which is free of time-reversal symmetry protected surface states at the conventional TRIM points, due to weak topological indices $Z_2 = (0;001)$. Moreover, we identify an additional protection of topological states with crossing points at non-TRIM points in the $\Gamma\overline{M}$ mirror plane direction governed by the crystal mirror-symmetry due to the non-zero mirror Chern number $n_{\text{M}} = -2$. This dual WTI and TCI character of time-reversal and mirror symmetry leads to the existence of topologically protected states on every surface of the crystal.

Confronting the theoretical predictions with the experiment, we successfully realized the thin film synthesis of Bi$_1$Te$_1$ on Si(111) by MBE-growth, carefully characterized the bulk crystal structure as well as the surface chemistry, and thoroughly investigated the electronic (spin-) structure. Indeed, we identified significant differences to the prototypical STI Bi$_2$Te$_3$ in the spin structure of the surface-related features at the Fermi level.
which is a good indication of the WTI nature of Bi₃Te₁. Furthermore, we unambiguously reveal mirror-symmetry protected band crossings at non-TRIM points which are in excellent agreement to theory and which we attribute to result from the TCI character of Bi₃Te₁. In future work, the weak topological nature of Bi₃Te₁ could be confirmed by probing the topologically protected one-dimensional electron edge channels at step edges of the dark surface, e.g. in a STS study (similar to what was reported in [19, 27, 28]). The dual topological character opens up new vistas for such materials in spintronics because topological states are protected by different symmetries and can be potentially switched on and off by breaking of a certain symmetry.

METHODS

Sample growth.

All samples for this study are grown as thin films via molecular beam epitaxy. Firstly, 10 × 10 mm² Si(111) samples were prepared by a RCA-HF procedure to remove organic contaminations and the native oxide. A consecutive HF dip passivates the Si surfaces with hydrogen for the transfer into the MBE chamber (base pressure 5 · 10⁻¹⁰ mbar). To desorb the hydrogen from the surface the samples were heated up to 700°C for 10 min and finally cooled down to 275°C. For the evaporation of Te and Bi, standard effusion cells were heated to T_{Te} = 260°C and T_{Bi} = 460°C, resulting in a growth velocity of Bi₃Te₁ of v = 2.5 nm/h. The tellurium shutter was opened several seconds in advance to terminate the silicon surface by Te, which saturates the dangling bonds. While Bi₃Te₃ is grown in a tellurium overpressure regime [29], Bi₁Te₁ requires equal vapor pressures of tellurium and bismuth. The 1:1 ratio between bismuth and tellurium changes the structure from solely quintuple layers in Bi₂Te₃ to a layered structure with additional Bi bilayers between every two QLs in Bi₁Te₁. After growth, the samples were transferred from the MBE chamber into the ARPES apparatus (< 1 · 10⁻¹⁰ mbar) without breaking the vacuum by an UHV shuttle with a base pressure below 1 · 10⁻⁹ mbar. The surface of such ‘as-grown’ samples is, due to the growth mode, expected to be Bi-poor, i.e., mostly QL-terminated. Nevertheless, the surface exhibit all three different terminations (see section II in the supplementary information).

Structural Characterization.

For characterizing the bulk crystal structure, XRD measurements were carried out, employing a high-resolution Bruker D8 diffractometer. Additionally, crosssectional specimen were measured in an aberration-corrected STEM with an electron beam of 0.8 Å (FEI Titan 80-200) for structural investigations on the atomic scale. For this, selected specimen are prepared by focused ion beam etching with firstly 30 keV and subsequently 5 keV Ga ions. Later Ar ion milling using the Fischione NanoMill was performed to reduce the FIB-induced damage. High-resolution STEM images made in high-angular annular dark field contain chemical information, since the contrast scales with the atomic number Z², allowing to distinguish between Bi and Te atoms.

Spectroscopy.

The lab-based high-resolution ARPES investigation was performed at T = 25 K with a MBS A1 electron spectrometer, using either non-monochromatized He Iα radiation of hν = 21.2 eV from a focused HIS 13 helium lamp or light from a microwave-driven MBS xenon discharge lamp producing hν = 8.4 eV photons. The beam spot size is about 400 μm in the former and 1 mm in the latter case and the light is unpolarized. The analyzer measures \(E_B\) vs \(k_{||,s}\) dispersion maps at once. Fermi surface mapping is achieved by rotating the sample with respect to the entrance slit of the spectrometer. The overall energy resolution is estimated to be 10 meV and the angular resolution is < 0.02 Å⁻¹. For spin-resolved ARPES measurements we used photons of hν = 22 eV a Scienta SES-2002 spectrometer and a Focus SPLEED polarimeter at beamline BL5 of the DELTA synchrotron in Dortmund at room temperature, resulting in an energy resolution of ≈ 100 meV [30]. Here, clean sample surfaces are prepared by sputtering and annealing after sample transfer through air, which resulted in Bi-rich sample surfaces (see section II in the supplementary information).

Electronic structure calculations.

The DFT calculations are performed for the bulk phase and thin films with three different surface terminations, namely a single and a double QL (1 and 2QL), and a Bi BL. The bulk unit cell consists of two QLs and one Bi BL, and the hexagonal atomic planes are all assumed to have a fcc-like (A-B-C) stacking. To simulate a Bi BL terminated surface, a symmetric 26 layer film with BL-QL-
QL-BL-QL-BL stacking was used. For the 1 and 2QL termination, symmetric 24 and 34 layer films were set up. We employ the full-potential linearized augmented plane wave method as implemented in the FLEUR code \[31\] with the relaxed lattice parameters from the Vienna ab-initio simulation package \[32, 33\]. The generalized gradient approximation of Perdew-Burke-Ernzerhof form \[34\] is used for the exchange correlation potential. Spin-orbit coupling is included self-consistently in the calculations. From the DFT calculations, we obtain structural parameters that are in good agreement with the experimental data. The size of the bulk unit cell in c-direction is 25.0 Å. It consists of two QLs of 7.48 Å thickness each and a Bi BL of 1.68 Å. The BL-QL separation is 2.66 Å and the distance between the QLS is 3.04 Å. At the surfaces, these distances contract slightly, e.g., the QL-QL distance decreases by 0.06 Å at the 2QL-terminated surface, while the QL-BL distance is reduced only by 0.04 Å for the 1QL termination. For BL termination, the interlayer distance changes even less. The step-height between a BL-terminated and a 2QL-terminated surface is thus 1.68 + 2.66 = 4.34 Å.

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