New three-dimensional (3D) topological phases can emerge in superlattices containing constituents of known two-dimensional topologies. Here we demonstrate that stoichiometric Bi$_1$Te$_1$, which is a natural superlattice of alternating two Bi$_2$Te$_3$ quintuple layers and one Bi bilayer, is a dual 3D topological insulator where a weak topological insulator phase and topological crystalline insulator phase appear simultaneously. By density functional theory, we find $Z_2$ indices (0;001) and a non-zero mirror Chern number. We have synthesized Bi$_1$Te$_1$ by molecular beam epitaxy and found evidence for its topological crystalline and weak topological character by spin- and angle-resolved photoemission spectroscopy. The dual topology opens the possibility to gap the differently protected metallic surface states on different surfaces independently by breaking the respective symmetries, for example, by magnetic field on one surface and by strain on another surface.
Topological insulators (TIs) are bulk insulating materials that exhibit metallic conductivity on their boundaries via electronic edge (in two-dimensional (2D) TIs) or surface states (in three-dimensional (3D) TIs), which are guaranteed by the topology of the bulk band structure. Electrons in these boundary states are spin polarized. Their spin and momentum are locked to each other by spin–orbit coupling, creating helical spin textures, which make TIs highly attractive for spintronic applications. One of the most favourable aspects of 3D TIs is the fact that their surface inevitably hosts these metallic surface states as long as the symmetry defining the topological index is not broken. In a strong TI (STI), time-reversal symmetry protects these states on all surfaces. Weak TIs (WTIs), on the other hand, display protected metallicity only at surfaces with a certain orientation, while other surfaces do not contain topologically protected surface states. The latter can be understood in a simple picture, where a stack of 2D TIs forms a WTI with metallic surface states inherited from the edge states of 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, metallic surface states can be found on surfaces perpendicular to these mirror planes.

Bi₂Te₃ was the first material predicted to be both a STI and a TCI. Since it exhibits two topological properties, it was termed a dual TI. Such a combination opens the possibility that controlled symmetry breaking would 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 by metallic surface states, that is, 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 caused by the WTI character, while the mirror-symmetry-protected states remain intact such that the dark surface is metallic. Likewise, small structural distortions can break the mirror symmetry without affecting the surface states arising from time-reversal symmetry, thus rendering only the dark side insulating.

In the search for such a material, we start from Bi₂Te₃ with the properties mentioned above and from the Bi bilayer (BL) which is known to be a 2D TI. It is possible to produce natural superlattices [Bi₂₆]ₙ[Bi₂Te₃]ₙ from hexagonal, metallic BLs and semiconducting Bi₂Te₃ quintuple layers (QLs) in a wide range of n and y. Within this series Bi₂Te₃ consists of QL building blocks, while the unit cell of Bi₂Te₃ exhibits a stacking sequence of a single BL interleaved with two subsequent QLs. The size of the unit cell along the stacking direction, that is, the c lattice constant, varies quite severely among the different stable compounds, which makes them easily distinguishable in a diffraction experiment. Recently, a similar superlattice Bi₈Se₉ (that is, x = y = 1) was investigated in some detail and characterized as a topological semimetal. For practical applications, however, an insulating bulk material is preferable.

In this article, we identify the stoichiometric natural superlattice Bi₁Te₁ (that is, x = 1, y = 2) as a semiconductor with a small bandgap of about 0.1 eV with the desired properties: Bi₁Te₁ is both a WTI and a TCI, and hence a novel type of dual TI with the favourable property of suitable surfaces as described above. Our density functional theory (DFT) calculations predict a Z₂ class of (001) and a mirror Chern number nₘ = −2. We find two characteristic surface states of the TCI on the (0001) surface, regardless of the surface termination. A similar situation has been reported recently for Bi₃TeI, theoretically. We demonstrate that Bi₁Te₁ can be grown in the 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), depicting a repeated stacking sequence of 2QL of Bi₁Te₁ and a single Bi BL. We investigate the electronic structure of Bi₁Te₁ by means of spin- and angle-averaged XRD, angle-resolved photoemission spectroscopy (ARPES), and angle-resolved electron energy loss spectroscopy (AERELS).

Figure 1 | Bulk band structures of Bi₁Te₁. (a) Simple sketch of the crystal structure of Bi₁Te₁. The unit cell consists of 18 Bi and 2 QLs. (b, d) The bulk band structure calculation in the structurally relaxed geometry (c) and with artificially expanded distances between the BL and the QLs (d), respectively. States localized mostly in the BL are marked in green, while the states localized mostly in the QLs are shown in red. In d, the band structure of the BL shows an inverted gap about 0.2 eV above the Fermi level (E₀ marked with a dashed line). (c) Bulk and surface Brillouin zone with parity product of the TRIM points for the relaxed structure resulting in +1 (red ‘+’) or −1 (blue ‘−’). The k₂ direction corresponds to the stacking direction. ΓAML, that is, (kₓ,k₂)-plane, marks a mirror plane.
resolved photoemission (spin-ARPES) on the (0001) surface. Our spectra taken along non-high-symmetry lines reveal band crossings away from time-reversal invariant momenta (TRIM) points that can be associated with surface states protected by mirror symmetry and the TCI character of Bi$_2$Te$_3$. Spin-ARPES reveals that the surface states surrounding $\Gamma$ and being close to $E_F$ exhibit a nearly vanishing spin polarization in contrast to the directly compared time-reversal symmetry-driven TSS in Bi$_2$Te$_3$ ($x=0$, $y=3$, $z$ is 3 here because the unit cell consists of three QLs), which is in line with WTI character with the dark surface being (0001).

Results

\textit{Ab initio} calculations. Figure 1a depicts a schematic model of the crystal structure of Bi$_2$Te$_3$, indicating Bi (green) and Te (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 BLs is marked. The bulk band structure of Bi$_2$Te$_3$ in the relaxed structural geometry is presented in Fig. 1b. Spin-orbit coupling is included in this calculation and the colour 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 \textit{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. 18 based on the product of the parities of all occupied bands at the eight TRIMs, that is, one at $\Gamma$, one at $A$, three at $M$ and three at $L$. The result is shown in Fig. 1c 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$_2$Te$_3$ is a weak TI 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 BL and the QLs 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. 1d, which introduce artificially expanded distances between the BL and the QLs, show a more complex scenario: if the BL is sufficiently separated from the QLs, the states can be decomposed into contributions from the two components (green = Bi BL and red = QLs, respectively). However, 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. 1b, as can be deduced from the changing colour 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$_2$Re$_3$I$_4$ (refs 19–21).

Next, we examined the surface band structure of 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, that is, 1Bi BL, 1QL and 2QL. Figure 2 depicts the spin-resolved surface band structure for the latter two terminations. In all cases an even number of Fermi level crossings is found in $\overline{TM}$ direction (see Supplementary Notes II and III for all terminations and convergence with film thickness). We observed that, although there are surface states, the band structure is compatible with the fact that we look at the dark surface of a WTI phase. Nevertheless, it is remarkable that the bands along $\overline{T}\mathbf{M}$ show a band crossing for all possible terminations, reminiscent of Dirac-like cones observed in TCIs. Additional evidence that this crossing is protected by a mirror symmetry in the crystal comes from the observation that the crossing is lifted when the surface atoms are displaced in [1100] direction, breaking this symmetry in one of the $\overline{T}\mathbf{M}$ directions (Fig. 2c).

To finally confirm that Bi$_2$Te$_3$ is a TCI, we determined the mirror Chern number of the bulk phase. In the ($k_x,k_y$) plane in reciprocal space (Fig. 1c) all Bloch states can be distinguished by their eigenvalues with respect to a mirror operation in the (1100) 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$^{22}$. 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 $n_M$ (ref. 6), given as $n_M = (n_{+i} - n_{-i})/2$, is $n_M = -2$. Confirming the fact that Bi$_2$Te$_3$ is a TCI. The modulus of $n_M$ shows that we have to expect two linear crossings along the high-symmetry line formed by the mirror- and the surface-plane$^{23}$, the sign determines the spin orientation$^6$ shown in the Supplementary Note II. The mirror Chern number $n_M = -2$ is incompatible with STI phase since it produces even number of crossings. In this context it might be interesting to note that the dual TI Bi$_2$Te$_3$ has $n_M = -1$, and consequently a single Fermi level crossing$^6$.

Let us discuss the individual features of the different terminations shown in Fig. 2 in more detail. The QL-terminated surface (Fig. 2b) shows near the Fermi level only the linear $\Gamma$-direction (Fig. 2c). It touches the bulk valence band along $\overline{T}\mathbf{K}$ and hybridizes with the protected surface state around $-0.1 \text{ eV}$ in $\overline{T}\mathbf{M}$ direction. The BL-terminated surface shows characteristic downwards dispersing states, very similar to features observed for a single BL on Bi$_2$Te$_3$ (refs 24,25), that are not seen in the experimental spectra shown below (calculations are presented in the Supplementary Notes II and III). All terminations show strongly spin-polarized surface states around 1.0 eV (Fig. 3a), which are similar to the Rashba-type surface states that also characterize the surface of Bi$_2$Te$_3$ (ref. 26) or Sb$_2$Te$_3$ (ref. 27).

Crystallographic structure. Figure 4 shows the experimental characterization of the bulk crystal structure of our Bi$_2$Te$_3$ thin films via XRD (Fig. 4a–c) and STEM (Fig. 4d). From the $\omega$ scans in Fig. 4a, the crystal phase was determined by comparing the peak positions with the calculated Bragg reflections, both for Bi$_2$Te$_3$ and Bi$_2$Te$_3$. The in-plane and out-of-plane lattice constants $a$ and $c$ were determined precisely from the reciprocal space maps around the $(1,0,-1,16)$ reflection for Bi$_2$Te$_3$ (Fig. 4b) and the $(1,0,-1,16)$ reflection for Bi$_2$Te$_3$ (Fig. 4c). The peaks were fitted with Gaussians for determination of the experimental error. We find $a = 4.37 \pm 0.12 \text{ Å}$ and $c = 30.51 \pm 0.46 \text{ Å}$ for Bi$_2$Te$_3$, and $a = 4.45 \pm 0.02 \text{ Å}$ and $c = 24.0 \pm 0.1 \text{ Å}$ for Bi$_2$Te$_3$.

In addition, the stoichiometries of the samples were also checked by Rutherford backscattering spectroscopy which confirmed the 50:50 ratio of Bi:Te (see Supplementary Fig. 1).

Figure 4d depicts a high-angular annular dark field image of a representative section of a 39-nm-thick Bi$_2$Te$_3$ film recorded by STEM. The observed clear contrast is related to the difference between individual atomic columns of Bi and Te (Bi atomic
Figure 2 | Spin-resolved DFT surface electronic structure calculations. Band structure along $\Gamma M K$ of slabs of $\text{Bi}_2\text{Te}_3$, terminated by (a) 2QLs and (b,c) 1QL. The size of the symbols corresponds to the spin polarization in the first four layers of a slab, the colour (red/blue) indicates the orientation of the spins with respect to a direction perpendicular to the momentum and surface normal. The green circle marks the Dirac cone of the TCI. In (opposite spin polarization for $\text{Bi}_1\text{Te}_1$) symmetry has been broken by strain along $[100]$, compared to Fig. 2, and by 250 meV for the $\text{Bi}_2\text{Te}_3$ case. Red arrows point to a single spin-polarized band in $\text{Bi}_2\text{Te}_3$ (b), and in $\text{Bi}_1\text{Te}_1$ (c,d) 2QL termination, and (e,f) 1QL termination, and superimposed on the experimental spectra in (g,h). The Fermi energy in the calculated spectra was shifted up by 100 meV (200 meV) in the 1QL (2QL) $\text{Bi}_1\text{Te}_1$ case compared to Fig. 2, and by 250 meV for the $\text{Bi}_2\text{Te}_3$ case. Red arrows point to a single spin-polarized band in $\text{Bi}_2\text{Te}_3$ (f), and two overlapping bands with opposite spin polarization for $\text{Bi}_1\text{Te}_1$ (j).

Figure 3 | Band structure of $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_1\text{Te}_1$. Comparative wide energy range ARPES spectra along $\Gamma K$ direction of thin films of (a) $\text{Bi}_2\text{Te}_3$ and (b) $\text{Bi}_1\text{Te}_1$ measured at $T=25\,\text{K}$ using $h\nu=21.2\,\text{eV}$. The colour code in the experimental spectra scales from bright = low to dark = high intensity. Superimposed are the results from the corresponding spin-polarized DFT calculations (1QL termination from Fig. 2 is used; red and blue dots mark opposite in-plane spin channels). (c,d) Energy distribution curves obtained along the dashed areas in (a,b) respectively, at (c) $k_{zx}=0\,\text{Å}^{-1}$ and (d) 0.39 Å⁻¹ (black curve from $\text{Bi}_2\text{Te}_3$ and green curve from $\text{Bi}_1\text{Te}_1$). Black arrows mark spectral dominant features. Magnified electronic structure close to the Fermi level along indicated crystallographic directions are shown in (e) for $\text{Bi}_2\text{Te}_3$ at $h\nu=21.2\,\text{eV}$ and in (h) for $\text{Bi}_1\text{Te}_1$ at $h\nu=8.4\,\text{eV}$. Additionally, the corresponding calculations are shown in (f) for $\text{Bi}_2\text{Te}_3$, and in (j) for $\text{Bi}_1\text{Te}_1$ (i) 1QL termination, (j) 2QL termination, and superimposed on the experimental spectra in (g,k), respectively. (k) shows overlap with (i) and (j). The Fermi energy in the calculated spectra was shifted up by 100 meV (200 meV) in the 1QL (2QL) $\text{Bi}_1\text{Te}_1$ case compared to Fig. 2, and by 250 meV for the $\text{Bi}_2\text{Te}_3$ case. Red arrows point to a single spin-polarized band in $\text{Bi}_2\text{Te}_3$ (f), and two overlapping bands with opposite spin polarization for $\text{Bi}_1\text{Te}_1$ (j).
columns appear brighter than Te columns). Distinct van der Waals gaps, separating QLs from BLs, are visible and the arrangement of BL and QL matches the expected 1:2 composition ratio. Furthermore, by extracting a line profile (yellow frame, which also defines the scale of the image) and fitting Gaussians to the peaks (green = Te; red = Bi) the atomic positions can be determined precisely. Using this method, the size of one bulk unit cell was confirmed to be $c = 23.99 \pm 0.02 \text{Å}$, which is in good agreement with the results from XRD.

As we have seen, due to the superlattice character of Bi$_1$Te$_1$, there is more than one possible surface termination, but neither XRD nor STEM probe the surface. Supplementary Notes II present a spectroscopic study of the chemical composition of the surface of Bi$_1$Te$_1$ and the influence of noble gas sputtering on the surface termination. It turns out that our growth conditions result in Bi-poor surfaces (that is, a higher amount of QL-terminated surface), while ion sputtering leads to Bi-rich surfaces (that is, a higher amount of BL-terminated surfaces). This is the reason why, in the following, we will mostly focus on 1QL- and 2QL-terminated Bi$_1$Te$_1$, since the samples that have been investigated by high-resolution ARPES (HR ARPES) were vacuum-transferred after growth and have never been exposed to ambient conditions.

However, since we expect differently terminated surface terraces to be in the order of few micrometer in size$^{16,28}$ and we employ beam spot sizes of 400 μm (HR ARPES) or even 1 mm (spin-ARPES) in the ARPES experiments, we have to assume that our electronic structure investigations always probe a superposition of different terminations. Therefore, due to the rich variety of surface-related states (Fig. 2) and the fact that our ARPES technique averages over the beam spot size, a detailed distinction of the surface electronic features is challenging.

### Surface electronic structure by ARPES

The comparative results of our ARPES investigations on vacuum-transferred, as-grown Bi$_2$Te$_3$ and Bi$_1$Te$_1$ thin films are summarized in Fig. 3. In the case of the prototypical STI Bi$_2$Te$_3$ our results reproduce earlier findings$^{26}$. In general, the spectra exhibit sharp features and a good signal-to-noise ratio revealing the high crystalline quality of the thin films. Figure 3a,b depict wide range binding energy $E_b$ versus wavevector $k_{\|,1}$ maps of Bi$_2$Te$_3$ (a) and Bi$_1$Te$_1$ (b), respectively, along trajectories in the $\Gamma K$ direction which traverse the $\Gamma$ point of the surface BZ, recorded with $h\nu = 21.2$ eV. Both samples are of $n$-type nature with the conduction band minimum being cut by the Fermi level.

On the first glance the spectra of the two samples show a lot of similarities but a closer analysis reveals some differences, as it can be best seen in energy distribution curves (Fig. 3c,d), which were plotted for $k_{\|,1} = 0 \text{ Å}^{-1}$ (Fig. 3c) (normal emission) and for $k_{\|,1} = 0.39 \text{ Å}^{-1}$ (Fig. 3d). The Bi$_1$Te$_1$ spectra globally seem to be downshifted which we attribute to a possible electron donation of the BLs to the QLs$^{16}$.

The spin-polarized surface electronic structure slab-calculations are superimposed onto the ARPES maps (for 1QL surface termination in the case of Bi$_1$Te$_1$). 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$_1$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 reasonable and most of the features can be matched.

Figure 3e–g, h–k show the comparison of the magnified electronic structure close to the Fermi level for Bi$_2$Te$_3$ and Bi$_1$Te$_1$, respectively. In Bi$_1$Te$_1$ (Fig. 3h) the predicted gap opening along $\Gamma K$ direction for 1QL termination is not reproduced in the experiment. However, the superposition (Fig. 3k) of the calculated spectra of 1QL (Fig. 3i) and 2QL-terminated Bi$_1$Te$_1$ (Fig. 3j) agrees well with the experimental spectrum where 2QL closes the gap. The gap opening in the surface state along $\Gamma K$ is expected since there is no mirror symmetry protecting the...
bands along this direction. Note, that the Fermi level in the 2QL-terminated calculation was shifted by roughly 100 meV more than in the 1QL case pointing to different charge transfer. Supplementary Note II depicts wider energy range simulations where one can see that the Fermi level of the 2QL-terminated case indeed needs to be shifted further to match the deeper lying intense Rashba-type features. Additionally, in Supplementary Note IV we analyse the photon energy dependence of the states

\[ \text{Binding energy (eV)} \]

The data from Bi₁Te₁ is compared to measurements on Bi₂Te₃ and the spin polarization of the prototypical TSS (Fig. 5d–f).

Figure 5a–d show the wide range ARPES maps of Bi₁Te₁ and Bi₂Te₃ from Fig. 3a,b, respectively, which illustrate along which opposing k-points, marked by the red dashed area, the spin polarization is measured. Figure 5b,c as well as Fig. 5e,f depict the wide range and near-Fermi level (in-plane) spin-resolved partial intensities I_{left} and I_{right} along the indicated k-points. The spectra were corrected by the asymmetry function, sometimes called the Sherman 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_F ≈ 3.2, ≈ 2.1 and ≈ 0.9–1.1 eV in Fig. 5b,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 Bi₂Te₃ shows a helical spin

\[ \text{Intensity (a.u.)} \]

Note IV we analyse the photon energy dependence of the states

\[ \text{Spin polarization} \]

This becomes apparent for the bands marked by

\[ \text{Different terminations simultaneously.} \]

In summary, we believe that we do not find a gap-opening in

\[ \text{In-plane spin polarization of 40–50% in the bands at higher binding energies, around E_F ≈ 3.2, ≈ 2.1 and ≈ 0.9–1.1 eV in Fig. 5b,e. The full reversal of the spin polarization between the two opposing k-points confirms the helical nature of these states in both samples. Further, the TSS of Bi₂Te₃ shows a helical spin} \]
polarization of up to 40% in Fig. 5f, which confirms its topological nature and is in agreement with what was reported earlier. On the contrary, Fig. 5c reveals that the most interesting states in Bi$_2$Te$_3$ at the Fermi level exhibit only very small (although non-vanishing) in-plane spin polarization of max. 10% without a clear reversal at the opposing k-points. Such weak spin polarization is expected due to spin–orbit coupling (Rashba effect) in the topologically trivial surface states (see states in the calculation in Fig. 3b,c). Therefore, this measurement reveals clear difference to the prototypical TSS and thus gives a strong experimental indication but no final proof for the non-topological character of these states at $E_F$ in Bi$_2$Te$_3$.

Finally, we describe our experimental evidence for the mirror-symmetry-protected band crossings at non-TRIM points, which are a consequence of the topological crystalline character of Bi$_2$Te$_3$. Figure 6 depicts experimental and calculated spectra along non-high-symmetry lines revealing TCI surface states. We identified significant differences to the electronic structure. We successfully realized thin films of Bi$_2$Te$_3$ on Si(111) by MBE growth, characterized the bulk crystal structure as well as the surface chemistry, and thoroughly investigated the (spin-) electronic structure. We identified significant differences to the prototypical STI Bi$_2$Te$_3$, that is, the spin polarization of the surface-related features at the Fermi level is negligible for Bi$_2$Te$_3$, which points to a non-topological character of this state, and,

**Discussion**

In summary, we predicted by DFT and demonstrated by ARPES the dual TI character of the stoichiometric natural superlattice Bi$_2$Te$_3$.

Our study theoretically predicts by *ab initio* DFT calculations that Bi$_2$Te$_3$ exhibits a dark surface perpendicular to the stacking direction which is free of time-reversal symmetry-protected surface states at the TRIM points, due to weak topological $Z_2$ indices $Z_2 = -2$. This dual WTI and TCI character leads to the existence of topological states on every surface of the crystal, which are protected either by time reversal or by mirror symmetries, respectively.

Confronting the theoretical predictions with the experiment, we successfully realized thin films of Bi$_2$Te$_3$ on Si(111) by MBE growth, characterized the bulk crystal structure as well as the surface chemistry, and thoroughly investigated the (spin-) electronic structure. We identified significant differences to the prototypical STI Bi$_2$Te$_3$, that is, the spin polarization of the surface-related features at the Fermi level is negligible for Bi$_2$Te$_3$, which points to a non-topological character of this state, and,
hence, is an indication of the WTI nature of Bi1Te1. Furthermore, 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, for example, 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 the 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.

It is well known that generalized gradient approximation overestimates the bond length in van der Waals-bonded systems. Therefore, we relaxed the structure also using the DFT-D2 method38 and obtained a slight contraction of the unit cell in c–direction. The resulting lattice constant of 24.0 Å is in good agreement with the experimental value while the topological features are unchanged.

Data availability. The data that support the findings of this study are available from the corresponding author on request.

References
1. Hasan, M. Z. & Kane, C. L. Colloquium: topological insulators. Rev. Mod. Phys. 82, 3045–3067 (2010).
2. Ando, Y. Topological insulator materials. J. Phys. Soc. Jpn 82, 102001 (2013).
3. Hsieh, D. et al. Observation of unconventional quantum spin textures in topological insulators. Science 323, 919–922 (2009).
4. Fu, L., Kane, C. & Mele, E. Topological insulators in three dimensions. Phys. Rev. Lett. 98, 106803 (2007).
5. Murakami, S. Phase transition between the quantum spin Hall and insulator phases in 3D: emergence of a topological gapless phase. New J. Phys. 9, 356 (2007).
6. Teo, J. C. Y., Fu, L. & Kane, C. L. Surface states and topological invariants in three-dimensional topological insulators: application to Bi–Sb. Phys. Rev. B 78, 045426 (2008).
7. Fu, L. Topological crystalline insulators. Phys. Rev. Lett. 106, 106802 (2011).
8. Rausch, T., Fleiger, M., Henk, J., Mertig, I. & Ernst, A. D. Dual topological character of chalcogenides: theory for Bi1Te3. Phys. Rev. Lett. 112, 016802 (2014).
9. Murakami, S. Quantum spin Hall effect and enhanced magnetic response by spin–orbit coupling. Phys. Rev. Lett. 97, 236805 (2006).
10. Wada, M., Murakami, S., Freimuth, F. & Bihlmayer, G. Localized edge states in two-dimensional topological insulators: ultrathin Bi films. Phys. Rev. B 83, 121310 (2011).
11. Yang, F. et al. Spatial and energy distribution of topological edge states in single Bi111 bilayer. Phys. Rev. Lett. 109, 016801 (2012).
12. Bos, I., Zandbergen, H., Lee, M.-H., Ong, N. & Cava, R. Structures and three-electronic properties of the infinitely adaptive series (Bi120xTe10x)2Sb2Te3. Phys. Rev. B 75, 195203 (2007).
13. Bos, I.-W., Fauch eux, F., Downie, R. & Marcinkova, A. Phase stability, structures and properties of the Bi120xTe10x,Bi2Te3 natural superlattices. J. Solid State Chem. 193, 13–18 (2012).
14. Cava, R. J., R. Fuccillo, M. K., Gibson, Q. D. & Hor, Y. S. Crystal structure and chemistry of topological insulators. J. Mater. Chem. C 1, 3176 (2013).
15. Isaeva, A., Rasche, B. & Ruck, M. Bismuth-based candidates for topological insulators: chemistry beyond Bi2Te3. Phys. Status Solidi RRL 7, 39–49 (2013).
16. Valla, T. et al. Topological semimetal in a Bi–Bi2Se3 infinitely adaptive superlattice phase. Phys. Rev. B 86, 241102 (2012).
17. Rusinov, I. et al. Mirror-symmetry protected non-TRIM surface state in the weak topological insulator BiTeI. Scientific Rep. 6, 20734 (2016).
18. Fu, L. & Kane, C. Topological insulators with inversion symmetry. Phys. Rev. B 76, 045302 (2007).
19. Pauly, C. et al. Subnanometre-wide electron channels protected by topology. Nat. Phys. 11, 338–343 (2015).
20. Rasche, B. et al. Stacked topological insulator built from bismuth-based graphene sheet analogues. Nat. Mater. 12, 422–425 (2013).
21. Pauly, C. et al. Electronic structure of the dark surface of the weak topological insulator Bi14Rh3I9. ACS Nano 10, 3995–4003 (2016).
22. Mostofi, A. A. et al. wannier90: a tool for obtaining maximally-localised Wannier functions. Comput. Phys. Commun. 178, 685–699 (2008).
23. Hirahara, T. et al. Interfacing 2D and 3D topological insulators: Bi(111) bilayer on Bi2Te3. Phys. Rev. Lett. 107, 166801 (2011).
24. Hao, L. et al. Quasiparticle dynamics in reshaped helical Dirac cone of topological insulators. Proc. Natl Acad. Sci. USA 110, 2758–2762 (2013).
25. Herde, A. et al. Spin-polarization limit in Bi2Te3 Dirac cone studied by angle- and spin-resolved photoemission experiments and ab initio calculations. Phys. Rev. B 87, 035127 (2013).
Acknowledgements

The authors acknowledge financial support from the priority program SPP1666 of the DFG (projects MU3187/3-1, RR23/2, and MO858/13-2) and the Virtual Institute for Topological Insulators (VITI) of the HGF. We thank Volkmart Hess, Samuel Königshofen, Frank Matthes and Daniel Bürgler for additional characterization of the surface chemistry of our samples in their laboratory-based XPS chamber. We also thank B. Hollander for the precise determination of the samples stoichiometry via RBS. Further, the authors acknowledge the technical support by B. Küpper and A. Bremen. The authors gratefully acknowledge the computing time granted on the supercomputer JURECA at Julich Supercomputing Centre (JSC).

Author contributions

M.E., Ma.La. and C.N. contributed equally to this work. Ma.La., P.S. and G.M. grew the samples via MBE. M.E., E.M., F.G., J.K. and L.P. carried out the lab-based HR ARPES experiments. C.N., G.B. and S.B. provided the ab initio DFT band structure calculations. M.E., M.G. and S.D. performed spin-resolved ARPES measurements at BLS of DELTA in Dortmund. Ma.La., E.N. and Ma.Lu. prepared the FIB lamellas and performed HR STEM measurements. G.M. characterized the samples by XRD. B.H. measured RBS for stoichiometry analysis. M.E., L.P., C.N. and G.B. wrote the paper with contributions from all coauthors. The project was supervised by M.M., S.B., D.G. and C.M.S.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Eschbach, M. et al. Bi1Te1 is a dual topological insulator. Nat. Commun. 8, 14976 doi: 10.1038/ncomms14976 (2017).

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/