Electronic structures of topological insulator Bi$_2$Te$_3$ surfaces with non-conventional terminations

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Abstract

Topological insulators (TIs) are theoretically believed to possess robust surface states (SSs) for any surface terminations. In reality, for TIs with non-conventional terminations, the directly experimental demonstration of this argument is somehow hindered, due to the difficulties in sample preparation and lack of efficient electronic structure characterization method. Here, by using the state-of-the-art molecular beam epitaxy, we manage to prepare TI Bi$_2$Te$_3$ thin film with non-conventional fractional quintuple layer (FQL) termination. Scanning tunneling microscopy reveals that the as-grown Bi$_2$Te$_3$ thin film may not necessarily terminate at the van der Waals gap between two adjacent quintuple layers. The electronic structures of the FQL termination are studied in combination with quasiparticle interference pattern by scanning tunneling spectroscopy and SS calculations by tight binding method. Our results suggest that the topological nature of SSs be preserved on various terminations. Possible ways of achieving exotic topological SSs are also discussed.

The idea of robustness of topological surface states (SSs) roots deeply in the fact of time-reversal invariant symmetry in topological insulators (TIs) [1–3]. Topological band theory has demonstrated the persistence of conducting SSs connecting the valence bands and conducting bands of TIs. Topological SSs have been proved to be crucial in the experimental realization of quantum anomalous hall effect (QAHE) [4, 5] and are believed to play important roles in many other quantum phenomena, such as magnetic monopole, Majorana fermions, topological superconductors, etc [6]. Thus many works have been devoted to investigate the topological nature of SSs, and most of them focus on the natural cleaving surfaces of TIs. However, researches on surfaces with non-conventional terminations are hindered due to the difficulties in preparation of those surfaces and the existence of a large number of dangling bonds. Therefore, only a quite limited number of works have been done, trying to illuminate the wonderland of those special surfaces of TIs [7–10].

TI Bi$_2$Te$_3$ has a rhombohedral crystal structure. Its unit cell contains five atomic layers with a stacking sequence of Te(1)–Bi–Te(2)–Bi–Te(1) along the [111] crystallographic orientation, which is defined as a quintuple layer (QL) as schematically shown in figure 1(a). We denote various possible surface terminations as S1–S5, where S1 is the conventional termination that can be experimentally realized by cleaving single crystal among the van der Waals gap [11, 12] or MBE growth of single crystal thin films [13, 14]. Theoretically speaking, non-conventional S2–S5 terminations could be artificially obtained by successively cleaving Te and/or Se layers (s) off from S1 termination. However, due to the strong valence bond interactions within the single QL and the weak van der Waals forces between two adjacent quintuple QLs, the naturally cleaved Bi$_2$Te$_3$ single crystals normally terminate at S1 surface. In this work, we manage to investigate the electronic structure of TIs Bi$_2$Te$_3$ surfaces with fractional QL (FQL) terminations by means of scanning tunneling spectroscopy (STS) and tight binding calculations. The sample was epitaxially grown on a Si(111)–7 × 7 substrate on our home-built MBE system with a base pressure better than $5 \times 10^{-10}$ mbar, following the well-established three temperature method [13]. Clean Si(111) substrate was obtained by annealing substrate at 450 °C for overnight followed by quick flashing to 1250 °C for several times. Bi (99.999%) and Te (99.999%) sources were evaporated from separate tungsten boat
which was heated by direct current. Flux rate of the sources was calibrated by commercial quartz crystal microbalance. During the sample growth, Bi and Te flux rate were kept at 0.060 Å s⁻¹ and 0.387 Å s⁻¹, respectively, and the Si substrate was kept at 260 °C. In our experiment, a Bi₁Te₃ thin film sample with a nominal thickness of ~40 nm was grown. The as-grown sample was transferred in-situ into our low temperature STM setup and the STM and STS experiments were undertaken at a temperature of 4.5 K and a vacuum pressure better than 1.0 × 10⁻¹¹ mbar.

Figure 1(d) exhibits a typical STM topography of our as-grown thin film. The vertical distance between the upper and lower terraces matches the height of 1 QL. These surfaces can be identified as termination S1. From the atomic resolution shown in the inset of figure 1(e), we find the step edge of those S1 terminations are dominantly oriented along the [100], [110] and [010] close packing directions. Besides those conventional S1-terminated regions, terraces with fractional QL termination were discovered by STM. STM topography of the region shown in figure 1(f) reveals the existence of three distinct terraces. From the line cross section shown in figure 1(g), the height of the middle terrace matches that of termination S4. To specifically identify the middle non-conventional terrace corresponds to S4 termination, we have the following consideration. Firstly, in the framework of s-wave type tip approximation, the tunneling current I(V) in STM experiments can be expressed as $I(V) \propto \int_{\epsilon_F}^{\epsilon_F + eV} \rho_1(\epsilon) \mathrm{d}\epsilon$, where $\epsilon_F$, $V$, and $\rho_1(\epsilon)$ correspond to Fermi energy, bias voltage and the density of state (DOS), respectively. As can be seen, $I(V)$ depends on the integration of the DOS from Fermi level to the energy level with a value of $eV$. For TIs Bi₁Te₃ that has a bulk energy gap of 165 meV, if $\epsilon_F$ and $\epsilon_F + eV$ both lie within the bulk gap, $I(V)$ varies with the detailed dispersion of the in-gap SSs. On the other hand, if $\epsilon_F$ and/or $\epsilon_F + eV$ lie(s) far away from the bulk gap, $I(V)$ will be dominated by contributions from the bulk DOS. As for figure 1(f), we used a bias voltage of 1.5 V, which is far away from the bulk gap of Bi₁Te₃. Therefore, $I(V)$ is determined by the bulk electronic structure of Bi₁Te₃, irregular to the detailed in-gap SSs. Therefore, in our case, $I(V)$ would perform the same behavior on the conventional (upper and lower) terraces and non-conventional (middle) terrace. In other word, the 'apparent' step height in figures 1(f) and (g) reveals the real step height, suggesting that the middle terrace be S4-terminated. Secondly, we have compared the STS spectra of the observed conventional and non-conventional terraces, as shown in figure 1(c) by red and blue spectra. The STS
The thin spectrum of S1 termination is consistent with that of pattern has been explained by a theoretical treatment based on the dispersions. However, a macroscopic large electronic structures of S1 and S4 terminations.

### Hexagonal Warping Effect

Bias voltage dispersed Dirac-cone like SSs on both terminations. The differences in slope and interpolated intersections with the electronic structure studies of non-conventional terminations of Bi2Te3. Hereafter, we mainly focus on the CEC of S1 termination, together with three possible scattering processes that are indicated by points on the CEC, would contribute the most weight in the power spectra. Figure 2 schematically shows the quantum interference between the incident and outgoing wave results in a standing wave pattern which has a spatial period of $2\pi/|q|$. The interference pattern can be investigated by STS mapping. Due to the hexagonal warping effect [17], the elastic scatterings between $k$ points with high DOS, i.e., concave extremal points on the CEC, would contribute the most weight in the power spectra. Figure 2(a) schematically shows the CEC of S1 termination, together with three possible scattering processes that are indicated by $q_1$ (red), $q_2$ (green) and $q_3$ (blue) [15, 18]. However, $q_1$ represents backscattering of $K_f$ to $K_i$, which is quantum mechanically prohibited in the absence of magnetic impurity. As for scattering wave vector $q_3$, its absence in the interference pattern has been explained by a theoretical treatment based on the $T$-matrix approach [18, 19], which shows that...
scattering weight of \( q_2 \) is approximately one order lower than that of \( q_2 \), due to the spin texture of the CEC.
Therefore, scattering wave vector \( q_2 \) dominates in the power spectra. The relationship between \( \vec{K} \) along \( \vec{\Gamma} \vec{K} \) and the scattering wave vector \( \vec{q} \) can be approximated as \(|\vec{k}| = |\vec{q}|/\sqrt{3}\). Therefore, as long as the evolution of \( q \) versus electron energies is known, the dispersion along \( \vec{\Gamma} \vec{K} \) can be directly determined. \( d\psi/d\psi \) mapping of S1 termination at 200 mV bias voltage is presented in figure 2(c). As expected, there exists sharp standing waves on the upper terrace. The standing waves propagate along \( \vec{\Gamma} \vec{M} \) direction, i.e., perpendicular to the step edge.

Figure 2(d) exhibits the corresponding local DOS (LDOS) oscillation as a function of the distance from the step edge, which can be well fitted by the decaying power law \( \delta \rho \propto \cos(qx + \phi)x^{-1} \), where \( q \) is the scattering wave vector. Due to the topological nature of TIs, we expect the existence of SSs on S4 termination and quantum interference pattern in STS experiments. Standing wave patterns were indeed observed in the STS mapping with 200 mV bias voltage on S4 termination, as shown in figure 2(e). The extracted LDOS oscillation as shown in figure 2(f) decays in the similar way as S1 termination, i.e., \( \sim x^{-1} \). To extract the band dispersion along \( \vec{\Gamma} \vec{K} \) in the SBZ, a series of \( d\psi/d\psi \) mappings were collected under various bias voltages and the scattering wave vectors \( \vec{q} \) were extracted by fitting the corresponding LDOS oscillations with the previous mentioned power decaying law. It should be stressed that the power indexes for various bias voltages do not necessarily equal to \(-1\). During the fitting, we also found the LDOS oscillations varied with \( \sim x^{-3/2} \), \( \sim x^{-1} \), and \( \sim x^{-1/2} \), and even a combination of those power indexes, which is consistent with the statement that the decaying law depends on the detailed topology of the CECs [20, 21]. However, the LDOS oscillation period for a given bias voltage does not varied with the power index, which makes it possible to extract the band dispersions from the standing waves. The extracted band dispersions along \( \vec{\Gamma} \vec{K} \) for S1 and S4 terminations are exhibited in figure 2(b) by solid circular and square scatters, respectively. At first glance, the resulting \( q \) varies linearly with energy. Fermi velocity of the Dirac fermion can be obtained by fitting the slope of the band dispersion, and the intercept of the linear fitting with the energy axis provide a measurement of the Dirac cone position. S4 termination has a greater Fermi velocity (3.79 eV Å) than S1 (2.04 eV Å), but has a lower Dirac point position (316 meV) than S1 (229 meV). The existence of standing waves and the linear dispersion on S4 indicate the existence of topological SSs on this particular non-conventional termination.

To have better knowledge of the electronic structure of S4 termination, we performed tight binding calculations. For our calculations, an approach similar to our previous work on TI Bi\(_1\ldots\), Sb, is introduced [8, 10]. The tight-binding parameters from [22] are used, in which second-neighbor hopping and spin–orbit coupling are included. The surface-state dispersions along high symmetric direction in the [111] SBZ are calculated in a slab scheme. A 20-QL slab structure is established to eliminate the electronic structure coupling between the upper and lower surfaces. As has already been mentioned in our previous work, this tight binding approach guarantees no accurate one-to-one resemblance to the first principle density function calculation. Nevertheless, for the purpose of investigating the topology of SSs and their robustness, it is quite straightforward and informative. In our calculations, the energy zero and Fermi level (\( E_f \)) are set to the valence band maximum and the center of the universal bulk band structure gap of Bi\(_2\)Te\(_3\), respectively.

Figures 3(a)–(e) show the band dispersions along \( \vec{K} \)–\( \vec{\Gamma} \)–\( \vec{M} \)–\( \vec{K} \) in the SBZ for Bi\(_2\)Te\(_3\) surfaces with S1–S5 terminations, respectively. The dense bands demonstrate the projections of the bulk band structures and a universal energy gap develops at \( E_f \) (indicated by blue dashed line). For S1 termination, the linear dispersed SSs reside in the bulk energy gap and form the notable Dirac cone. And the Dirac point lies slightly above the valence band maximum at \( \vec{\Gamma} \) but 220 meV below \( E_f \) which agree well with previous calculations and experiments [11, 12, 23]. For S4 termination, there exist SSs in the bulk band gap, too. The SS along \( \vec{\Gamma} \vec{M} \) connects the valance and conduction band continuum, which guarantees the robustness and topological nature of the SSs on S4 termination. The SSs on S4 span a larger \( k \)-space in the SBZ, which results in a smaller Fermi velocity along \( \vec{\Gamma} \vec{K} \) than that of S1 termination. This calculation results is contrary to our STS mapping results in which the Fermi velocity of S4 is greater than that of S1 along \( \vec{\Gamma} \vec{K} \). However, this deviation is somehow expected, as no surface construction or relaxation is taken into consideration in our tight binding method. Cleavage other than the conventional S1 termination would normally result in the variation of the bonding environment and hopping parameters in the first few atom layers, and the corresponding SS dispersions would vary accordingly. Despite this discrepancy, we find the Dirac point on S4 termination merges into the conduction continuum and is lower than that of S1 termination, which is consistent with our STS experimental results.

As for S2 termination (figure 3(b)), the SSs are a bit complicated. There is also a set of Dirac cone at the SBZ center. What is more, another set of Dirac cone like SSs emerge at \( \vec{M} \) point, i.e., the other time reversal invariant momentum in the SBZ. However, this additional Dirac cone is trivial compared to the one at \( \vec{\Gamma} \), as the SSs that form this Dirac cone both merge into the valence band continuum at certain \( k \)-points between \( \vec{\Gamma} \) and \( \vec{M} \) and could be tuned into the bulk continuum by variation of chemical potential or external perturbations. Therefore, S2 termination has a single non-trivial Dirac cone in the SBZ. With the similar argument, S1–S5 terminations all have equivalent SSs topology, despite the fact that their SSs disperse quite differently. It should be noticed that the Dirac point positions vary with different terminations as shown in figure 3(f). The Dirac point on S2...
termination locates almost at Fermi level \( (E_f) \), while those of S4 and S5 termination merge into the bulk valence and conduction continuum, respectively. The physics behind the different features of SSs would most likely reside in the deformation of Hamiltonian in the formation of those various terminations. Taking S4 termination for example, we can see from previous experimental and tight binding results that its Dirac point merges into the valence bulk continuum and is lower than that of S1 termination. S4 termination could be constructed on both sides of a 20 QLs slab to eliminate the SSs of S1 termination, with the resultant slab structure in the form of –Bi–Te–QLs–Te–Bi–. This structure could be considered either as cleaving the remaining –Te–Bi–Te– part of a QL away (i.e., removing process), or adiabatically moving the –Bi–Te– structure from infinity toward the 20 QLs slab (i.e., the adding process). Let us focus on the adding process. The Dirac point position for the 20 QLs slab is around 140 meV below the zero energy (valence maximum), while the SSs intercepts at Gamma point with a binding energy of around 400 meV for the –Bi–Te– structure (calculation result not shown here). Thus it is quite straightforward that while the two structures are brought together, the resultant SSs would have a Dirac point position that is lower than S1 termination, but hight than the –Bi–Te– structure. Actually, this situation is similar to the cases of Bi–xSb\(_x\) [24], Pb–1-xSn\(_x\)Se [25], Bi\(_{2\text{-}x}\)Sb\(_{x}\)Te\(_{1\text{-}y}\)Se\(_y\) [26], where the tailoring of the topological nature of their SSs and Dirac cone(s) is resulted from the continuous deformation of the Hamiltonian by variations in the tailoring parameters (i.e., concentrations of doping elements). The situation for other non-conventional terminations could be considered in the similar way.

As many novel physical phenomena such as QAHE, topological superconductivity, etc, occurs when the Dirac point pins at Fermi level, our calculation results suggest a possible way in the engineering of SSs in TIs. Novel topological SSs might be achieved by creating non-conventional terminations of the well-known TIs. The efficient tight binding calculation could be directly applied to other TI systems, and the preliminary topological nature and Dirac cone topology of the SSs on various terminations could be easily established. Thereafter, based on those results, SSs with better performance could be sorted out with the aid of further first principle calculations. An important issue that arises is the experimental realization of the non-conventional terminations and the verification of their SS topologies. Here in our work, we have paved a way of solving this issue by means of MBE growth and STS mapping techniques. In order to pratically apply our techniques to control the topological SSs, different terminations of TIs should be seperately fabricated and characterized. In fact, terraces with sub-QL height (measured from the substrate) that resembled S3 and S4 terminations were observed by STM at the initial stage of MBE growth of Bi\(_2\)Te\(_3\) thin films, i.e., during the formation of the first Bi\(_2\)Te\(_3\) QL [27].

![Figure 3.](image-url)
Technically speaking, additional S3 and/or S4 terminations could most likely be fabricated separately on as-grown Bi2Te3 thin films with conventional S1 terminations, by fine tuning of the deposition time and/or adjustment of Bi/Te flux ratio and substrate temperature. Additionally, exotic SSs might emerge by MBE growth of TIs on single crystal substrates with non-conventional crystalline indices, such as Bi(110), Bi(114), Bi(441), etc.

Acknowledgments

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