Scanning tunneling microscopy study of the possible topological surface states in BiTeCl

Y J Yan, M Q Ren, X Liu, Z C Huang, J Jiang, Q Fan, J Miao, B P Xie, F Xiang, X Wang, T Zhang and D L Feng

1 State Key Laboratory of Surface Physics, Department of Physics, and Advanced Materials Laboratory, Fudan University, Shanghai 200433, People’s Republic of China
2 Collaborative Innovation Center of Advanced Microstructures, Fudan University, Shanghai 200433, People’s Republic of China
3 Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials (AIIM), University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW 2500, Australia

E-mail: tzhang18@fudan.edu.cn, dlfeng@fudan.edu.cn, xiaolin@uow.edu.au and fx963@uowmail.edu.au

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Abstract

Recently, the non-centrosymmetric bismuth tellurohalides such as BiTeCl are being studied as possible candidates for topological insulators. While some photoemission studies showed that BiTeCl is an inversion asymmetric topological insulator, others showed that it is a normal semiconductor with Rashba splitting. Meanwhile, first-principle calculations have failed to confirm the existence of topological surface states in BiTeCl so far. Therefore, the topological nature of BiTeCl requires further investigation. Here we report a low-temperature scanning tunneling microscopy study on the surface states of BiTeCl single crystals. On the tellurium (Te)-terminated surfaces with relatively low defect density, evidence for topological surface states is observed in the quasi-particle interference patterns, both in the anisotropy of the scattering vectors and the fast decay of the interference near the step edges. Meanwhile, on the samples with much higher defect densities, we observed surface states that behave differently. Our results may help to resolve the current controversy on the topological nature of BiTeCl.

Keywords: topological surface states, BiTeCl, non-centrosymmetric

Topological insulators (TIs) are bulk insulators with metallic surface (edge) states protected by time-reversal symmetry [1, 2]. This intriguing state was theoretically predicted and experimentally observed in a variety of 2D and 3D systems with strong spin-orbital coupling (SOC) [3–7]. TIs have brought forward new and exotic physics such as magnetic monopole [8] and Majorana fermions [9]. So far, most of the discovered TIs are centrosymmetric. However, when inversion symmetry is absent in TIs, more unusual topological phenomena and practical applications can be realized, such as crystalline-surface dependent topological states, intrinsic topological p-n junctions [10, 11], and the topological magneto-electric effect [12]. Therefore, the search for inversion asymmetric TIs has recently attracted much interest.

The layered compounds BiTeX (X = Cl, Br, I) are of growing interest for their strong SOC and lack of lattice inversion symmetry. Large Rashba spin splitting (RSS) is widely observed in these compounds, which may facilitate future spintronics applications [13–17]. Moreover, a recent angle-resolved photoemission spectroscopy (ARPES) study revealed that BiTeCl cleaved in vacuum exhibited surface states with Dirac cone-like dispersion, implying that it is possibly a topological insulator without inversion symmetry [18]. However, the emergence of a topological phase in BiTeCl was not found in first-principles...
calculations [15], and some other ARPES works on BiTeCl only observed parabolic bands with RSS, instead of a Dirac cone [16, 17]. Therefore, whether the surface state in BiTeCl has a topological origin and how the unexpected TI phase emerges are still open issues, which require further investigation.

Scanning tunneling microscopy (STM) is a surface sensitive tool which played important role in the discovery of TIs [19–21] (a surface p-n junction was observed on BiTeI by STM recently [22, 23]). In this paper, we report first a STM study on the surface states of BiTeCl. In the sample with relatively low defect density, we observed surface state-induced interference patterns on the Te-terminated surface. The scattering intensity is concentrated along the \( \Gamma - \bar{M} \) direction, which resembles the classical topological insulator Bi\(_2\)Te\(_3\). Moreover, the decay of the standing waves around the step edges is much faster than those of conventional surface states. By comparing with previous ARPES results and simulated scattering patterns, the observed surface states are likely of topological origin. More interestingly, in the sample with higher (about 5 times) defect density, we observed surface states with different scattering patterns. This implies that a band structure mutation may happen with increased bulk carriers, which tend to screen out the surface polarization.

Single crystals of BiTeCl were grown by a self-flux method, as described in 23. The crystal structure of BiTeCl is shown in figure 1(a), characterized by the alternative stacking of the Te, Bi, and Cl layers along the c-axis. Each atomic layer is arranged in a triangular lattice. This crystal structure is confirmed by x-ray diffraction (XRD) (figure 1(b)) with the lattice constants \( c = 12.39 \) Å. Different batches of samples with various carrier densities were studied. The typical temperature dependence of the resistivity is shown in figure 1(c), which displays a metallic behavior similar to that reported before [16]. The STM experiments were performed in a cryogenic STM system at 4.5 K. Samples were cleaved at a low temperature of 77 K in vacuum of \( 1 \times 10^{-10} \) torr, in order to get a fresh surface without contamination and to reduce the possibility of generating unexpected surface defects during the cleaving process. The samples were transferred to the STM module immediately after cleaving. Pt tips were used after treatment on the Au (1 1 1) surface. Bias voltage \( V_b \) was applied to the sample with respect to the tip, and the tunneling spectroscopy (\( dI/dV \)) was collected using a lock-in method with a modulation frequency of 975 Hz.

It is known that the cleavage of BiTeCl happens between the Te and Cl layers, leaving a pair of polarized Te- and Cl-terminated surfaces [18]. In our STM measurement we only observed two kinds of surface terminations, as shown in figures 1(d) and (e). Judging from their topographic and spectroscopic characters (as shown throughout this paper), we attributed figure 1(d) as a Te-terminated surface and figure 1(e) as a Cl-terminated surface. The Te-terminated surface is atomically flat with several tip categories, as marked in the top-left corner in figure 1(f). The center of the triangle is at the hollow site of the Te lattice, thus the type I defect is possibly caused by substituting a Te atom at the Bi site (Te\(_{Bi}\)) [20]. Te\(_{Bi}\) defects are electron donors, which is consistent with the n-type nature of bulk BiTeCl [16, 24]. The averaged defects density (including all kinds of defects) for the surface shown in figure 1(d) is about \( 2 - 3 \times 10^{12} \) cm\(^{-2}\). If all the observed defects belong to the topmost Te-Bi-Cl tri-layer, the corresponding bulk defect density will be \( 3 - 5 \times 10^{19} \) cm\(^{-3}\). Samples with higher defect densities are also studied, which will be discussed later. For the Cl-terminated surface the topography is much rougher with randomly distributed clusters and stripe-like features. This could be due to the strong polarization of this surface [15]. Figure 1(g) displays the tunneling spectroscopies (\( dI/dV \)) taken on the two surfaces, which gives a measurement of the local density of states (LDOS). For the Te-terminated surface, a rather V-shaped LDOS is observed in between \(-200 \sim -700\) meV, with a minimum at \(-600\) meV. This feature is consistent with the existence of a Dirac cone [6, 20]. The possible onsets of bulk conduction and valence bands are indicated by the arrows in figure 1(g). As for the Cl-terminated surface, the averaged \( dI/dV \) spectrum shows a gap-like structure from \(-400\) meV to \(100\) meV. Because of the bad surface condition, we did not do
To further study the electronic states, we performed dI/dV mappings on the Te-terminated surface. Figures 2(a)–2(f) show representative dI/dV maps at various Vb measured in the same region, as shown in figure 1(d). A marked feature is that pronounced interference patterns (or standing waves) can be observed in the vicinity of the defects. It is known that such a quasi-particle interference (QPI) pattern is caused by the scattering between the initial and final states at the same constant energy contour (CEC) in the momentum space. The corresponding wavevectors are \(k_i\) and \(k_f\), respectively, and the scattering vector is given by \(q = k_f - k_i\). Pronounced interference usually comes from 2D states because the bulk (3D) states would give continuous ranges of \(q\) on the projected surface Brillouin zone (SBZ) and cannot generate distinct interference. In figures 2(g)–2(l), we show the 2D Fourier transformation (FT) of figures 2(a)–2(f), in which the scattering intensities with various \(q\) s can be revealed (the 2D FTs are six-fold symmetrized to raise the signal to noise ratio). The SBZ is superposed in figure 2(g) to help orient the scattering directions. One finds that the \(q\) vectors make up an anisotropic ring, the size of which shrinks as Vb decreases, indicating that the scatterings are from an electron-like surface band. The regions with high scattering intensity are along the \(\Gamma - \Delta\) directions. Figure 2(m) shows the line cuts that are extracted along \(\Gamma - \Delta\) in all of the FT maps (displayed in a gray scale).

The \(E\) versus \(q\) dispersion can be clearly visualized. Further deciphering the FT patterns requires detailed knowledge of the band structure. As mentioned earlier, ARPES studies have observed two kinds of surface bands in BiTeCl, which are: (i) A Dirac cone-like surface band with the Dirac point (DP) at \(\approx -560\) meV [18]; (ii) Rashba split parabolic bands with the band bottom at \(\approx -450\) meV [16, 17] (note that 18 also observed parabolic bands in some cases, which they ascribed to single-layer BiTeCl flakes). Below we will distinguish which one is actually observed here.

The topological Dirac cone and Rashba split surface bands both have spin textures on their CEC. For scatterings that preserve time-reversal symmetry, the intensity of a specific \(q\) can be calculated by the spin-dependent joint density of states (SJD):

\[
SJD(q) = \int T(k, q) |I(k)|^2 d^2 k.
\]

\(I(k)\) is the intensity of an electronic state with \(k\) at a certain CEC, as directly measured by ARPES. \(T(k, q) = \langle S(k)|S(k + q)\rangle\) is the matrix element when considering the spin states of the initial and final states. The calculated SJD image in q-space then provides a simulation of the FT images obtained by QPI. At the energy range where we observed interference patterns (\(-300 \sim 100\) meV), the CECs of both cases (i) and (ii) deviate from a circular shape due to the warping effect (from
the high order term of the SOC that reflects the surface crystal symmetry) [25, 26]. We calculated the SJD corresponding to these two cases. For case (i), the CEC actually resembles the classical topological insulator Bi$_2$Te$_3$ and the band structure can be described by the effective Hamiltonian with a warping term [25]:

$$H(k) = E_0 + v_F(k_x \sigma_y - k_y \sigma_x) + \frac{\lambda}{2}(k_x^3 + k_y^3)\sigma_z.$$

Figure 2(n) shows the simulated CEC at $E = -50$ meV to reproduce the ARPES result in 18 (We chose $E_0 = -0.56$ eV, $v_F = 2.65$ eV Å, and $\lambda = 60$ eV Å$^3$). The CEC is a warped hexagon [18], the valley points (along $\Gamma - \nu$) are better separated from the bulk bands than the ‘tip’ points (along $\Gamma - \overline{M}$) and the valley points have a higher DOS, as observed in 18. Thus, the scatterings are expected to be dominated by $q$ vectors that connect valley points, as marked by $q_1 \sim q_3$. It has been demonstrated in Bi$_2$Te$_3$ that due to the spin chirality of the Dirac cone, scatterings at $q_1$ are suppressed for the opposite spin orientations, $q_3$ is also weakened for its nearly opposite spin orientations [25, 27]. Thus the dominant scattering vector is $q_2$, which connects the ‘stationary points’ along the $\Gamma - \overline{M}$ directions [29]. The calculated SJD pattern in figure 2(o) also gives a high intensity direction along $\Gamma - \overline{M}$, qualitatively agreeing with the data. A full T-matrix calculation of the scattering for this case is reported in 27, which gives a similar FT pattern. For case (ii), the CEC is composed of two (inner and outer) Rashba bands, which can be described by the following effective Hamiltonian proposed in 26:

$$H(k) = E_0 + \frac{k_0^2}{2m^*} + v_c(1 + a_ck^2)k_x \sigma_y - k_y \sigma_x + \lambda(3k_x^2 - k_y^2)k_x \sigma_z.$$

Figure 2(p) shows the CEC at $E = 0$ meV to reproduce the Rashba bands observed in 16. (We chose $m^* = 22.1$ eV Å$^2$, $E_0 = -0.52$ eV, $v_c = 1.15$ eV Å, $a_c = -41$ Å$^2$, $\lambda = 30$ eV Å$^3$). Here because the inner and outer sub-bands have opposite spin chirality, the dominant scattering vectors will be the ones connecting the two sub-bands (marked as $q_4$ and $q_5$). However, although the CEC has anisotropy, the calculated SJD pattern (figure 2(q)) does not show significant enhancement along $\Gamma - \overline{M}$. Therefore, based on the above simulations, the anisotropic interference supports that the surface states have a topologically nontrivial origin, rather than a normal 2D states with Rashba splitting.

As shown in figure 2(n), $q_2$ is about $\sqrt{3}$ times of the $k$ along $\Gamma - \overline{M}$ ($k_{TR}$). Thus, we can extract the band dispersion $E-k_{TR}$ from figure 2(m). The results are shown in figure 3(k). A linear fitting gives a slope ($v_F$) of 2.34 eV Å and an intercept.
of $E_d = -580 \text{ meV}$ (which is the location of Dirac point). Both $V_F$ and $E_d$ qualitatively agree with the topological surface states observed by ARPES in 18.

Besides point defects, atomic steps on the cleaved surface can also induce scattering that contains information on the topological nature of the surface states. Figure 3(a) shows a step edge formed along the [101] direction (which is perpendicular to the close packing direction of the surface atom lattice). We mapped an area next to the upper step edge that has no point defects (as marked in figure 3(a)). The $dI/dV$ mappings in figures 3(b)–(h) show that standing waves clearly form around the edge, but decay quickly away from the edge. For conventional surface states, it is known that the decay of the standing wave intensity away from the edge follows the power-law: 

$$I(q) \propto |q|^p$$

with an index $p$ of $-1/2$ [28]. But as recently discovered, if $q$ is a vector which connects opposite spin states (for example, the backscattering vector of topological surface states), the decay will be faster with $p = -3/2$ [29]. Thus, the decay behavior will give another clue to distinguish the topological surface states. In our case, $q$ is along [1 1 2], which is the $\Gamma - \bar{K}$ direction in the $k$ space. For the CEC displayed in figure 2(a), the dominant $q$ along $\Gamma - \bar{K}$ is $q_1$, which is exactly the backscattering vector that connects opposite spin states. For the CEC shown in figure 2(p), $q_4$ is the backscattering vector along $\Gamma - \bar{K}$ but connects the states with the same spin orientation. So the decay in case (i) will follow $p = -3/2$, and for case (ii) the decay will be the same as conventional surface states with $p = -1/2$. Figures 3(i) and (j) show two representative fittings of the line profiles extracted from $dI/dV$ maps, corresponding to $V_b = -250 \text{ meV}$ and $-50 \text{ meV}$. Both of them can be better fitted with a decay index of $p = -3/2$ (red curves) than $p = -1/2$ (black dashed curves).

Thus, this is the second piece of evidence to substantiate that we observed topological surface states. Because $q_1 = 2k_{\Gamma K}$, we can also extract the $E-q$ relation from the mappings near a step edge, as shown in figure 3(k). The $E-k_{\Gamma K}$ obtained by two different ways basically match with each other.

If BiTeCl is a topological insulator, the question is why it was not reproduced in previous theoretical calculations. As discussed in 18, a possible reason is that the vacuum-cleaved surface is polarized (unpassivated), which will induce an electrical field near the surface. The electrical field and the effective pressure generated by the field may significantly alter the bulk band structure. A topological transition is thus possible under these conditions [26]. A recent transport measurement also reports a possible topological phase transition of BiTeCl under high pressure [30]. In our measurement, the clean Te-terminated surface supports the polarization

![Figure 4](image-url)

Figure 4. QPI patterns on the Te-terminated surfaces with a higher defect density. (a) Topographic image of the Te-terminated surfaces with a surface defect density of $1.2 \times 10^{13} \text{ cm}^{-2}$. (b) Averaged $dI/dV$ spectrum taken on the Te-terminated surface with a high defect density (red) compared to the one measured on the surface in figure 1(d) (black). (c)–(i) The $dI/dV$ maps at various $V_b$. Each map has 250 x 250 pixels. (j)–(n) The FTs of the $dI/dV$ maps in (c)–(i). (c) The line cuts extracted from the FTs along $\Gamma - \bar{M}$, shown in the gray color scale. (d) Red spots: $E-q$ relation extracted from panel (c) here. Gray spots: $E-q$ relation extracted from figure 2(m).
assumption. On the other hand, the intrinsic defects (as shown in figure 1(d)) should provide bulk carriers, which will weaken the surface polarization-induced electrical field through screening. Thus, one may expect that if there are sufficient defects, the topological surface states might vanish due to the change of band structure. So far, we have presented data taken on the surface with a defect density of $2 \sim 3 \times 10^{12}$ cm$^{-2}$. However, we also studied the samples with higher defect density (the variation of defect density is due to the slightly different growth condition). Figure 4(a) shows a Te-terminated surface with a much higher defect density of about $1.2 \times 10^{13}$ cm$^{-2}$. The most common defects are still clover-shaped ones. The $dI/dV$ maps on this surface and their FTs are shown in figures 4(e)–(i) and figures 4(j)–(n), respectively. The line cuts taken along $\Gamma - \text{M}$ of the FTs are summarized in figure 4(c). One finds that the interference patterns also exist, but their FTs are less anisotropic and more blurred when compared with those in figure 2. This could be due to the increased number of defects suppressing the electron coherence and weakening the interference. However the $E-q$ dispersion is still visible in figure 4(c). As shown in figure 4(d), the $E-q$ relation extracted from figure 4(c) is clearly different from the $E-q$ relation extracted from figure 2(m). At first, figure 4(d) appears to indicate a rigid band shift between the two surfaces, that is, the $E_F$ of the sample with a higher defect density shifts downwards. However, if the type I defects are electron donors, more defects should shift $E_F$ upwards. This discrepancy implies that there might be a band structure mutation instead of a rigid band shift. In figure 4(b), we show the tunneling spectrum measured on this surface. It is significantly different from the V-shaped spectrum measured on the surface in figure 1(d). In this regard, we propose that the surface states in figures 4(e)–(i) may be attributed to normal surface states instead of a topological Dirac cone. In figure 4(d), we show that a parabolic fitting of the $E-q$ gives a band bottom at $\sim 310$ meV. However, because the high density of defects also affect the resolution of the QPI, direct comparisons between the FTs and simulations (such as the one in figure 2(q)) are difficult here. More experimental and theoretical works are needed to understand this possible topological phase transition.

In summary, we have studied the surface states on the Te-terminated surface of BiTeCl by low-temperature STM. On the surface with a relatively low defect density, the anisotropic scattering patterns and faster decay of the standing waves along the atomic step edges strongly suggest that the surface states have a topological nontrivial origin. On the other hand, the surface states observed on samples with higher defect densities might be attributed to the topological trivial states observed in some ARPES measurements. Our results help to resolve the current discrepancy in the ARPES studies of BiTeCl, and also suggest the possible causes for the emergence and disappearance of topological surface states, and thus a possible path to tune the topological transition in such materials.

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