Topical Review

Advances in bismuth-based topological quantum materials by scanning tunneling microscopy

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Abstract
In recent years, topological quantum materials (TQMs) have attracted intensive attention in the area of condensed matter physics due to their novel topologies and their promising applications in quantum computing, spin electronics and next-generation integrated circuits. Scanning tunneling microscopy/spectroscopy (STM/STS) is regarded as a powerful technique to characterize the local density of states with atomic resolution, which is ideally suited to the measurement of the bulk-boundary correspondence of TQMs. In this review, using STM/STS, we focus on recent research on bismuth-based TQMs, including quantum-spin Hall insulators, 3D weak topological insulators (TIs), high-order TIs, topological Dirac semi-metals and dual TIs. Efficient methods for the modulation of the topological properties of the TQMs are introduced, such as interlayer interaction, thickness variation and local electric field perturbation. Finally, the challenges and prospects for this field of study are discussed.

Keywords: STM/STS, topological quantum materials, bismuth, spin–orbit coupling

1. Introduction

In recent decades, the exploration of topological quantum materials (TQMs) has evoked tremendous interest in condensed matter physics, which has benefited from the rapid development of theoretical and experimental endeavors to understand their novel electronic topologies. To date, there has been a huge family of TQMs, including topological insulators (TIs), topological crystalline insulators (TCIs), topological semi-metals (TSMs), and topological superconductors [1, 2]. These TQM-based electronic devices possess great potential applications. In fact, TIs exhibit robust boundary states, which possess spin-momentum locked electrons and survive under moderate disorder as a consequence of their electronic wavefunctions, representing a promising candidate for spin-based spintronics and quantum computers [3, 4]. Based on the Bernevig–Hughes–Zhang model, different topological classes can be achieved by controlling the band inversion between the conduction and valence bands with different band parities and strong spin–orbit coupling (SOC) [5]. The strong SOC normally provides a large band inversion energy, which is essential for the modulation of topological properties and potential applications, as shown in figure 1. For example,
Moreover, the ‘robustness’ of the TES can be verified by the zero in the range of the insulating energy gap (figure 6). However, for the bulk state of TIs, the LDOS remains boundary due to the 1D topological edge state (TES) in the measurement system, and scanning tunneling microscopy, and an outlook based on this research to attempt to propose a viewpoint of the experimental part of the realization of novel TQMs as well as their practical applications.

Future perspectives
The experimental realization of novel topological quantum materials (TQMs) including strong topological insulators, weak topological insulators, quantum spin Hall insulators, quantum anomalous Hall insulators and topological semi-metals, has been extensively explored to catch up with the development of topological theories in recent decades. The gap between the applications and the fundamental properties of these TQMs is their stability in the environment of their practical use, where the thermal perturbation at room temperature may break the topological surface/edge states. Seeking new materials with a large topological gap or modulating the existing TQMs in various ways, such as element doping, strain effect, electric/magnetic field and light, is regarded as an effective path to promote their applications. This paper provides a brief overview of the bismuth-based TQMs studied by experimental technique, scanning tunneling microscopy, and an outlook on the prospects for monolayer Bi(111) on Bi substrate (figure 3(f)–(h)).

There are several kinds of techniques to investigate the electronic features of TQMs, including angle-resolved photoemission spectroscopy (ARPES), a physical property measurement system, and scanning tunneling microscopy (STM). Among them, STM is of particular interest because of its unique atomic-spatial resolution to characterize the local density of states (LDOS), which is perfectly suitable to identify the bulk-boundary correspondence of low-dimensional TQMs. The experimental setups for the STM technique are shown in figure 2(a). After applying a bias voltage and controlling the distance between the tip and the sample of around 0.3–0.7 nm, the tunneling current can be detected after the preamplifier. The topography of the sample can be acquired by maintaining the tunneling current at a constant value and recording the distance between the tip and sample at different sites. Meanwhile, scanning tunneling spectroscopy (STS), namely the differential conductance spectrum (dI/dV), can be acquired using the standard lock-in technique with a small bias voltage modulation applied to the sample. It is noted that the measured dI/dV is proportional to the LDOS and as a result, for 2D TIs, the LDOS is a nonzero constant at the boundary due to the 1D topological edge state (TES) in the gap. However, for the bulk state of TIs, the LDOS remains zero in the range of the insulating energy gap (figure 2(b)). Moreover, the ‘robustness’ of the TES can be verified by the response of edge states to face small-size barriers, such as point defects, disorders and vacancies, in the STM measurements. The band structure dispersion cannot be directly measured using the STM technique, but can be achieved using the ARPES technique.

In this review, we focus on STM studies of electronic properties of Bi-based TQMs. The advances in the monolayer Bi, bismuthene, with various crystalline structures are first reviewed to illustrate the relationship between their electronic structures and interface interactions with underlying substrates. Then, we discuss the role of Bi in the topological properties of the Bi-based components within the halogen family and alkali metals. Different methods to change the topological properties of these TQMs are discussed to reveal an effective way to realize different topology classes. Finally, we include an overview of the general outlook and challenges in this field.

2. Bismuthene
In recent years, bismuthene, monolayer Bi, has been explored with different allotropes, including bilayer Bi(111), Bi(110) and single-layer Bi films with strong interaction with the underlying substrate [6, 11–14]. Compared to other 2D elemental materials, bismuthene is expected to demonstrate a high probability of band inversion and consequent large gap due to strong SOC. Nevertheless, bismuthene cannot naturally exist because of the non-van der Waals interlayer interaction. Thus, bismuthene can be artificially fabricated using a nondynamic equilibrium technique, such as molecular beam epitaxy (MBE).

2.1. Bi(111) bilayer
Single-layer Bi(111), the (111) plane of the Bi-rhombohedral structure [15], possesses a low-buckled honeycomb structure with Bi atoms alternatively buckled up and down, as shown in figure 3(a), forming two nonequivalent sublattices with a height difference. Therefore, single-layer Bi(111) is treated as the Bi-bilayer. The Bi-bilayer theoretically represents an elemental 2D TI, i.e. QSHI, according to the Kane–Mele model [16]. An energy gap (∼350 meV) and helical edge state can be seen in the monolayer Bi (111), as calculated by density functional theory (DFT) and shown in figure 3(b). Experimentally, a Bi-bilayer has been successfully fabricated on the surface of Bi₂Te₃ substrate (figure 3(c)) with the edge state appearing in the energy window from 136 to 370 mV, as shown in figure 3(e) [6]. The edge state is reflected by the peak in the STS curves, where the peak position is independent of the sample position (figure 3(e)), excluding the possibility of standing edge waves. The topologically nontrivial nature of the observed edge state is supported by the decaying width of the edge state (∼2 nm) in (figure 3(d)), which is much longer than the length of the boundary dangling bonds. Furthermore, all the data, including the DFT, ARPES and STS results for monolayer Bi(111) on Bi₂Te₃ substrate (figures 3(f)–(h)) reveal an edge state in the bulk energy gap, indicating...
Figure 1. (a)–(c) Schematic of the band structure of 2D normal insulators (NIs), Dirac semimetals (DSMs) and TIs, i.e. QSHIs, respectively. $k_x$ and $k_y$ represent the reciprocal lattice vectors of 2D Brillouin zone. Upper yellow bands and lower green bands represent 2D bulk bands, and the 1D red and blue lines in (c) are denote the 1D TES. (d)–(g) Schematic of the band structure on the top and side surfaces of 3D NIs, DSMs, WTIs, and STIs, respectively. Upper yellow bands and lower green bands represent the projection of 3D bulk bands to 2D surfaces, while the 1D red and blue lines in (f), (g) represent the 2D surface states.

Figure 2. (a) Schematic of STM/STS experimental setups for 2D TIs. Red and blue lines represent the helical edge state of TIs. The tip can be placed at bulk (A) or edge (B) sites to detect the LDOS differences between TIs. (b) Electronic structure and corresponding LDOS at site A and B of 2D TIs, where A and B in (b) represent the bulk and edge sites in real space, as depicted in (a), respectively. For 2D TIs, the LDOS is a nonzero value in the gap due to the existence of the TES.
Figure 3. (a) Schematic of crystal structure of the bilayer Bi(111). Reproduced with permission [39]. Copyright 2018, American Physical Society. (b) Band structure of the free-standing Bi(111) zigzag edge nanoribbon with the helical edge state in the energy gap. (c) Edge step of one Bi(111) bilayer on the Bi₂Te₃ substrate. (d) STS mapping at 283 mV corresponding to panel (d). (e) Line STS curves along the blue line in panel (d). Red dots mark the position of TES. (f) Calculated band structure of one bilayer Bi(111) on Bi₂Te₃ substrate. ‘DP’ marks the Dirac point in the valence bands. (g) ARPES results for one bilayer Bi(111) on Bi₂Te₃. (h) STS acquired at the terrace (red line) and edge (blue line) of one bilayer Bi(111), averaged over the area as marked in the inset. Reproduced with permission [6]. Copyright 2012, American Physical Society.

the topological properties of the Bi(111) layer. It is noted that the energy gap (∼76 meV) marked by orange dashed lines in figures 3(f)–(h) is much smaller than in the free-standing monolayer Bi(111) in figure 3(b), demonstrating the interface interaction between Bi(111) and the underlying substrate on the topological properties.

2.2. Bi(110)

The freestanding Bi(110) layer adopts a puckered structure, as shown in figure 4(a), forming the distorted black phosphorus structure with variable $h$. Bi(110) thin films can be acquired by depositing Bi on highly oriented pyrolytic graphite (HOPG) or Si(111) substrate with less than four layers [17, 18]. Although a previous report implied a topologically trivial feature of Bi(110) thin film [19], the STM/STS experimental results combined with DFT calculations revealed that the buckling degree of the top two type-Bi atoms could modulate the topological properties of Bi(110) thin films from topological non-triviality to triviality [13]. A flattened Bi(110) with a thickness of two monolayers (MLs) and four MLs (figure 4(b)) can be obtained after depositing Bi atoms on the HOPG substrate, with $h = 0$ resembling the black phosphorus structure. Moreover, the relationship between the energy gap and the sublattice height difference $h$ of the two ML Bi(110) films is calculated, where the energy gap is determined by the $h$
(figure 4(c)). When $h < 0.1 \text{ Å}$, the SOC-induced band inversion is identified, resulting in a nontrivial topology of Bi(110). The STS curves in figure 4(d) reveal the energy gap and the related TES. The energy gap closes at $h = 0.1 \text{ Å}$, where the topological phase transition (TPT) occurs. With a further increment in $h$, the energy gap reopens, and the band structure turns out to be a topological triviality (figures 4(e)–(h)). In experiments, the different values of sublattice height difference are expected to be controlled by the interface interactions between Bi(110) and different underlying substrates. Therefore, seeking suitable substrates to accommodate Bi(110) thin films is regarded as an effective way to modulate their topological properties.

2.3. Bismuthene on SiC

The interaction between 2D materials and underlying substrates is regarded as a useful means to change the crystalline structures and electronic features of 2D materials. Planar honeycomb bismuthene has been fabricated on a Si-terminated SiC(0001) substrate, as shown in figures 5(a)–(c), where the hybridization of $p_z$-orbitals of Bi atoms with the bottom substrate is identified, pushing the $p_z$-orbitals out of the low-energy region [14]. Consequently, the electrons near the Fermi level in bismuthene on SiC substrate are mainly contributed by $p_x$-orbitals and $p_y$-orbitals (figure 5(d)). In addition, their large on-site SOC directly determines the magnitude of the
energy gap rather than the SOC between nearest neighbors of $p_z$-orbitals under the second-order perturbation theory in the graphene case, leading to the formation of the largest topological nontrivial energy gap of 0.8 eV (figures 5(e)–(g)). A large bulk energy gap from $-0.2$ to 0.6 eV can be clearly seen in the line STS (figure 5(h)) collected at a position far away from the edge. As the tip approaches the edge, the DOS increases gradually, which means that it is a conductive 1D edge state. However, according to the theoretical prediction, the edge state is expected to have a linear dispersion relation that possesses a constant DOS under different energy levels. The point STS near the edge exhibits a pronounced dip near zero bias voltage, which is correlated to Tomonaga–Luttinger liquid (TLL) behavior. Stühler et al [20] carried out their experiments by measuring the edge states at different temperatures (from 10 to 100 K). The results are well fitted by using the TLL model (figure 5(i)). The TLL behavior can also be observed in other topological 1D edge channels [21], where
the electrons are confined in a narrow space and the correlation between the electrons becomes remarkable. Consequently, the interaction between electrons is the origin of the suppression of low-energy tunneling.

3. Quasi-1D \( \text{Bi}_I \text{X}_4 \) (\( X = \text{I}, \text{Br} \))

3.1. Epitaxial growth of \( \text{Bi}_I \text{X}_4 \) nanoribbon

The most promising feature of QSHI is the 1D edge state, which can serve as a dissipative conducting channel and candidate for the applications of quantum computers. The building block of \( \text{Bi}_I \text{X}_4 \) (\( X = \text{I}, \text{Br} \)) is 1D molecular chains stacking along the direction of both the \( c \)-axis and \( a \)-axis via van der Waals force (figure 6(a)). Based on the first-principles calculations, the authors observed in figure 6(f), where a non-zero but gap-like black curve, with finite DOS residing in the gap energy region with a energy ranging from \(-200\) to \(160\) meV and the ‘V-shape’ red curve, with finite DOS residing in the gap can be observed. The finite DOS is evoked by the TES. The STS mapping results (figure 6(f)) reveal a \(~1.5\) nm width of the decaying length of the edge state, which is comparable to the decaying length of the TES observed in other QSHIs [14, 24–26]. Combined with first-principles calculations, the authors demonstrated that the observed edge state can be ascribed to the existence of the topologically nontrivial nature of \( \text{Bi}_I \text{I}_4 \) monolayer.

3.2. Surface electronic structure of \( \text{Bi}_I \text{Br}_4 \) single crystal

Bulk \( \text{Bi}_I \text{X}_4 \) can be treated as a self-supported substrate for monolayer \( \text{Bi}_I \text{X}_4 \) due to the weak van der Waals interaction along the \( c \)-axis. Moreover, the weak interlayer interactions can preserve their intrinsic topological properties. The crystal structure and electronic properties of the cleaved (001) surface of \( \text{Bi}_I \text{Br}_4 \) single crystal have been studied using the STM and ARPES methods [27]. A large area of \( \text{Bi}_I \text{Br}_4 \) (001) with a smooth surface was acquired on the bulk substrate by cleaving the single crystal. Atomical sharp edges are observed in figure 6(h), where the line STS along the direction perpendicular to the edge exhibits a large gap around \(0.2\) eV and the edge state residing in the gap energy region with a \(1.7\) nm decaying length, as shown in figure 6(i). The gap value and position are consistent with the ARPES results. Combined with first-principles calculations, the gap has been identified to be a quantum spin Hall gap with band inversion at the \( M \) point of the Brillouin zone (BZ), revealing the topological nontriviality of the edge state. With the increment in temperature, the chemical potential is shifted, leading to the Lifshitz transition and the Fermi level in the gap region at room temperature. It should be noted that the gap value shows a weak dependence with the change in temperature, preserving the quantum spin Hall gap of \(~0.2\) eV and consequently promising the potential application of this material in electronic and spintronic devices to overcome thermal perturbations at room temperature. The temperature-dependent ARPES results are consistent with the temperature-dependent STS mapping results, where the TES survives at room temperature due to the large energy gap and atomically sharp edge [28].

4. WTI: \( \text{Bi}_I \text{Rh}_3 \text{I}_9 \)

The WTIs, 3D allotropes of 2D QSHIs, can be formed by stacking 2D QSHIs along the out-of-plane direction with weak interlayer interactions [29]. Theoretically, WTIs possess even numbers of band inversions at different time-reversal invariant points. Consequently, topological surface states in a WTI emerge on a particular side surface, and the top surface of a WTI can be treated as a layer of QSHI. Bi-based WTIs, which have been supported by experiments, include \( \beta-\text{Bi}_I \text{I}_4 \) and \( \text{Bi}_I \text{Rh}_3 \text{I}_9 \). The former was verified by the ARPES experiments carried out by Noguchi et al [30]. We review the topological properties of \( \text{Bi}_I \text{Rh}_3 \text{I}_9 \) that have been explored using STM/STS methods.

\( \text{Bi}_I \text{Rh}_3 \text{I}_9 \) consists of two types of alternately stacked layers, i.e. \([\text{Bi}_I \text{Rh}_3 \text{I}_9]^{2+} \) layer that was predicted to be a 2D TI and \([\text{Bi}_I \text{I}_4]^{-2} \) layer that serves as a trivial spacer (figure 7(b)) [31]. The STM image of the cleavage surface of \( \text{Bi}_I \text{Rh}_3 \text{I}_9 \) (figure 7(a)) exhibits two different layers that can be identified with different layer heights. The 2D TI layer exhibits a graphene-like honeycomb lattice, and the trivial spacer layer forms a hexagonal arrangement of iodide ions in STM images (figures 7(d) and (c)). There are several types of QSHIs, while their 3D allotropes are not concluded in WTI due to the existence of interlayer interaction even in a weak van der Waals force. However, the 2D TI layer in \( \text{Bi}_I \text{Rh}_3 \text{I}_9 \) is intercalated by the spacer of the trivial \([\text{Bi}_I \text{I}_4]^{-2} \) layer to further weaken the interlayer interaction. Moreover, the trivial layer exhibits a gap feature in the energy region of the quantum spin Hall gap and TES in the 2D TI layer, as shown in the STS curves in figure 7(f), resulting in there being no electronic states from trivial layer hybrids with the TES in 2D TI. The pronounced peak in the gray curve (figure 7(f)) indicates a TES of the 2D TI layer, and the STS mapping in figure 7(h) under a bias of \(-250\) mV displays a DOS distribution in real space (figure 7(g)), where the robust TES distribution along the edge is artificially created by the atomic force microscope.

5. STI: \( \text{Bi}_2 \text{Te}_3 \)

The family of \( A_2B_3 \) (\( A = \text{Bi}, \text{Sb}; \ B = \text{Te}, \text{Se} \)) topological materials in 3D STI has attracted intensive studies in recent
decades [32–34]. The crystal structure of the $A_2B_3$ family is shown in figure 8(a), where a quintuple layer with $B$–$A$–$B'$–$A''$–$B''$ is indicated by the red square. A single Dirac cone on the (001) surface can be found in the bulk insulating gap calculated by DFT (figure 8(b)) [35]. In contrast to WTI with partial surface states, STIs possess completely conductive topological surface states, where back-scattering is prohibited due to spin-momentum locking. Using the STM and STS methods, Zhang et al [36] investigated the STS mapping on Bi$_2$Te$_3$ and the corresponding scattering wave vector in momentum space, which provided convincing evidence for the lack of backscattering of electrons on the surface of a 3D TI. In their experiments, high-quality Bi$_2$Te$_3$ thin films were grown using the MBE method, and a few Ag trimmers were deposited on the top surface to serve as a non-magnetic scattering center (figures 8(d) and (e)). Figures 8(f)–(j) display various standing
Figure 7. (a) Large-area STM image of the cleaved Bi$_{14}$Rh$_3$I$_9$ surface. Inset is the height profile along the green line. (b) Schematic of Bi$_{14}$Rh$_3$I$_9$ crystal structure. Red cells are [(Bi$_4$Rh)$_3$I]$_2^+$ and the blue cells represent [Bi$_2$I$_8$]$^-$. Atomically resolved image of (c) [(Bi$_4$Rh)$_3$I]$_2^+$ layers and (d) [Bi$_2$I$_8$]$^-$ layers, respectively. (e) Step edge between [(Bi$_4$Rh)$_3$I]$_2^+$ and [Bi$_2$I$_8$]$^-$ layers. (f) Point STS measured at the points marked in panel (e). (g) STM image and (h) STS mapping of 2D TI layer. STS is taken under bias voltage of $-250$ mV. Reproduced with permission [31]. Copyright 2015, Springer Nature.

Figure 8. (a) Crystal structure of Bi$_2$Se$_3$ family. Primitive cell is marked by black lines. (b) Band structure of Bi$_2$Te$_3$ from first-principles calculations. Reproduced with permission [35]. Copyright 2009, Springer Nature. (c) Constant energy contour of the band structure of the Bi$_2$Te$_3$(111) surface. Red arrows represent the possible initial and final vectors of the quasi-particle. (d) STM image of an area with four Ag trimmers adsorbed on the Bi$_2$Te$_3$(111) surface. (e) Adsorption site of Ag trimmer. (f)–(j) $dI/dV$ mapping in the same area as (d) at different bias voltages. (k)–(o) Corresponding FFT power spectra of the $dI/dV$ mapping in (f)–(j). Reproduced with permission [36]. Copyright 2009, American Physical Society.
waves induced by four Ag trimmers on the Bi$_2$Te$_3$ top surface under different bias voltages. The fast Fourier transform (FFT) (figures 8(k)–(o)) of the $dI/dV$ maps in figures 8(f)–(j) reflects the component of the scattered wave vector ($\vec{q}$). It is found that the wave vector in $\vec{q}$ space mainly consists of only one direction, namely $\Gamma$–$M$. The results can be understood by investigating the constant-energy contour of the band structure of Bi$_2$Te$_3$. Figure 8(c) exhibits the three main kinds of possible scattering wave vectors in the reciprocal space, namely $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$. The scattering wave vector observed in experiments is $\vec{q}_2$, and the $\vec{q}_1$ represents the back-scattering vector and, as a result, is prohibited.

6. HOTIs: bulk bismuth, $\alpha$-Bi$_4$Br$_4$

HOTIs have been proposed as an extension of topological classification according to the $Z_4$ topological index [37]. The bulk-boundary correspondence in second-order TIs is that a $(d-2)$-dimensional gapless boundary state. For instance, conductive channels emerge only on the 1D hinge of a 3D HOTI, while their bulk and surfaces maintain an insulating state. The high-order topology proposed in Bi-based materials was verified by experiments that include the bulk bismuth [8] and $\alpha$-Bi$_4$Br$_4$ [38].

Bulk bismuth has been regarded as a topologically trivial material under the $Z_2$ criterion before the notion of HOTI was proposed. Some experimental results indicate that the 1D conductive edge state survives in thick Bi(111) films and bulk bismuth, and its origin is explained as a TES of 2D QSHI [7, 39]. The STM/STS technique combined with theoretical calculations and transport measurements reveals the nontriviality of bulk bismuth. The conventional unit cell (red line) and primitive unit cell (black line) are shown in figure 9(a), which exhibit three-fold rotational ($C_3$) symmetry and spatial inversion symmetry. Theoretical analysis indicates that the bulk bismuth holds the conductive hinge states. These hinge modes are simultaneously protected by time-reversal symmetry, $C_3$ symmetry and spatial inversion symmetry. Figure 9(b) shows the band structure of the bismuth with inversion eigenvalues (green) and $C_3$ eigenvalues on the $\Gamma$–$T$ line (black). A hexagonal pit was found in an STM topography image, and the location of hinge models is drawn as purple lines. The red and blue arrows represent the spin-momentum locked flow. The differential conductance map in figure 9(d) exhibits a good agreement with figure 9(c) and supports the theoretical prediction that bulk bismuth is a HOTI.

Recently, $\alpha$-Bi$_4$Br$_4$ was theoretically predicted to be a HOTI, where the conductive channel emerges only on the
Figure 10. (a) Schematic of the crystal structure of Bi$_2$TeI. (b) Bi(111) bilayer in the bulk Bi$_2$TeI and its TES in the energy bands. (c) Bulk band structure projected into the top surface of Bi$_2$TeI is protected by crystal symmetry. (d) Cleaved surfaces of Bi$_2$TeI obtained using STM. (e) Schematic of the exposed surfaces and steps corresponding to panel (d). (f) STS mapping measured along the gray line in panel (d). (g) Point STS curve acquired at the position marked by blue and black arrows in panel (f). Inset shows the gap opening due to the mirror-symmetry breaking near the step. (h)–(j) Point STS curves obtained at different positions marked in panel (e). Reproduced with permission [43]. Copyright 2020, Springer Nature.

hinge between the (001) surface and the (100) surface. Noguchi et al [38] reported an investigation on the topological properties of crystal $\alpha$-Bi$_4$Br$_4$ using their laser ARPES equipment. Due to the lack of spatial resolution for ARPES methods, the origin of the edge states observed in their experiments needs to be further confirmed by allying with other experimental techniques. Using the STM/STS methods with high spatial resolution, Shumiya et al [28] studied the DOS difference at the two kinds of edges due to the possible hybridization of edge states between two adjacent layers.

7. Dual topological material: Bi$_2$TeI

Dual topological materials possess two classes of topologies. Recently, a few dual topological materials have been proposed and have been identified in experiments [40–42]. Bi$_2$TeI was reported to exhibit dual topology with the properties of WTI and TCI on the top surface [43]. The crystal structure of Bi$_2$TeI is shown in figure 10(a), in which a single Bi(111) bilayer is stacked in the middle of two layers of BiTeI. It has been revealed by experiments that the Bi(111) layer is a QSHI, as
discussed above. Bi₂TeI holds the properties of WTI due to the weak coupling between Bi(111) layers and the intercalated BiTeI layer, similar to the case of Bi₁₄Rh₃I. There are two Dirac cones located at the Z point and Γ point of the BZ, respectively. Both Dirac cones project to the cleavable surface with an energy deviation, which is expected to be hybridized with each other and opens an energy gap without the protection of symmetry. The mirror symmetry of the crystal leads to Bi₂TeI, a TCI, and protects a degenerate nodal line at the intersection points, as shown in figure 10(c). The STM topography image of the cleaved surface of Bi₂TeI is depicted in figure 10(d), where three kinds of surfaces are exposed. The LDOS (figure 10(f)) measured along the gray line in figure 10(d) shows metallic properties throughout the surface with partial suppression of DOS next to the step edges (figure 10(g)), which is caused by the opening of an energy gap of Dirac cones due to the mirror-symmetry breaking at the step edges. The WTI nature is demonstrated by the measured DOS at different edges. The topological 1D channel appears only at the edge of the terrace terminated by a bilayer Bi(111) (5–6, figure 10(j)) and the LDOS of the edges of two other types of edges (3–4, figure 10(h); 4–5, figure 10(i)) does not exhibit any increase in the in-gap energy.

8. Topological Dirac semi-metal (TDS) and TPT in Na₃Bi

TDS, a counterpart of graphene in 3D form, has attracted significant interest in recent years [44–47]. The band structure of the 3D TDS can be regarded as a 3D Dirac cone in 4D space, and its projection to the 3D space can be attributed to a graphene-like 2D cone (figures 11(a)–(c)). Moreover, 3D TDS is a critical topological state similar to many other topological materials, such as Weyl semi-metal, trivial insulator, TI, axion insulator, etc. Na₃Bi is predicted to be a 3D TDS, which has been verified by ARPES experiments [9]. The crystal structure of Na₃Bi is shown in figure 11(d) with van der Waals interlayer interaction. Similar to graphene, the quasi-particle interference (QPI) phenomenon (figure 11(e)) has been observed [48] in the surface of Na₃Bi by STS mapping under different
energies, where an isotropic Fermi velocity in both directions perpendicular to the cleavage plane, which is expected for a 3D TDS, can be deduced.

The TPT can be induced by varying the thickness of Na$_3$Bi films [49] or applying an external electric field to the ultrathin Na$_3$Bi layers [50]. A transition from semi-metal to TI occurs when the thickness of Na$_3$Bi films decreases from bulk to four layers or fewer (figure 11(f)). The topological nature of ultrathin Na$_3$Bi films grown using the MBE method has also been modulated by the tip electric field. The strength of the electric field is controlled by doping potassium on the surface or approaching the STM tip. The gap closing and reopening can be clearly identified in the point STS curves (figure 11(g)) with the increase of tip electric field from 0.83 – 1.18 V nm$^{-1}$, where the monolayer or bilayer Na$_3$Bi experiences a TPT from nontriviality to triviality. The large insulating gap under a low electric field suggests a promising topological transistor for room-temperature applications in the future. The TPT induced by an electric field has special significance in applications due to the electric on-off being widely adopted in electronic devices, such as chips.

9. Magnetic topological materials: MnBi$_{2-x}$Sb$_x$Te$_4$

The intrinsic magnetic topological insulator, MnBi$_2$Te$_4$, has attracted significant attention in recent years due to its coexisting inherent magnetic order and topologically nontrivial band structure [51]. Crucial quantum states, such as the quantum anomalous Hall effect, axion insulating state, Weyl semi-metal state, and other exotic states depending on the magnetic order configuration were observed in this material [52]. The structure of single-layer MnBi$_2$Te$_4$ is displayed in figure 12(a), which has septuple layers of Te–Bi–Te–Mn–Te–Bi–Te stacking order. The phase transition from antiferromagnetic (AFM) order to paramagnetic order occurs at 24.2 K (Neel temperature), and the AFM order comes from the oppositely aligned magnetic moment of interlaminar Mn layers. MnBi$_{2-x}$Sb$_x$Te$_4$ is an STI in the system, implying that a surface state with Dirac cone dispersion can be seen on the (0001) surface. After the AFM order is turned on, a magnetic gap is opened at the Dirac point. Experimentally, the surface state was mainly investigated using the ARPES method in previous studies, where the gapped and gapless surface spectra were observed.
Figure 13. (a) Four building blocks that consist of a large family of the Bi-based TQMs. Blue solid (orange dash) arrows connecting two blocks represent the reported (unreported) compounds stacked by the two corresponding blocks. (b)–(d) Schematic of different stacking orders of the existing topological materials consisting of building blocks connected by a blue solid line in panel (a).

simultaneously, leading to an inconclusive value of the magnetic energy gap [53, 54].

Ko et al [55] reported band structure of MnBi$_{2-x}$Sb$_x$Te$_4$ (MBST) measured using the STM/STS method with QPI patterns. The bulk MnBi$_2$Te$_4$ exhibits an electron-doped band structure, and the Fermi level is tuned into the bulk band gap by substituting Bi with Sb elements without changing the AFM order of the ground state. The atomic STM topography of the cleaved (0001) surface of MBST ($x = 0.64$) is shown in figure 12(b), in which many defects can be observed. The Fermi level moves from the conductive band ($x = 0$), residing in the bulk band gap ($x = 0.64$), to the valence band ($x = 2$), as shown in the point STS curves of three samples (figure 12(c)). The QPI images in figures 12(d)–(f) reflect the detailed evolution of the band structure in MBST samples. When $x = 0$, a topological surface state can be clearly seen in the bulk band gap. However, the magnetic gap is not large enough to be identified due to the strong background of bulk scattering wave vectors. As the Sb substitutes the Bi with $x = 0.64$, a magnetic gap of around 50 meV is formed in the topological surface state. In contrast, no surface state is found in the bulk band gap of the $x = 2$ compound, indicating a topologically trivial insulator for MnSb$_2$Te$_4$.

10. Conclusion

In this review, we provide a brief introduction to the development of Bi-based TQMs from the point of view of both theoretical simulations and experimental methods of the STM technique. Compared to other techniques, such as ARPES, STM is a powerful tool to identify topological electronic features at high spatial resolution, which is ideally applied to characterize the topological surface/edge states in TQMs. Furthermore, the tunneling current between the tip and sample can be used as an external factor to modulate the topological properties of these TQMs. The strong SOC provides a large energy to induce the band inversion, and consequently results in a large topological nontrivial gap. However, the highest temperature of the quantum spin Hall effect detected by transport experiments is 100 K [24], which is a long way from room temperature. There are three factors determining the survival temperature of the quantum spin Hall effect: a large energy gap to overcome the thermal perturbation, atomic sharp edges to minimize the scattering and a long coherent length to promise the electron interference. The STM results reveal that Bi$_4$Br$_4$ is QSHI with a large energy gap and atomic sharp edge, according to the first two factors to realize the high-temperature quantum spin Hall effect. Thus, transport measurements of high-quality monolayer Bi$_4$Br$_4$ are expected to solve this mystery.

It is noticeable that most of the Bi-based TQMs can be made up of four building blocks: Bi bilayer, Bi$_2$(Se,Te)$_3$, BiTeX ($X = Cl, Br, I$) and MBi$_2$Te$_4$ ($M = Pb, Sn, Ge, Mn$), as shown in figure 13(a) [56]. These and their 3D allotropes possess different topological properties, and their combinations reflect abundant topological features. The materials comprising Bi and Bi$_2$(Se,Te)$_3$ include BiSe, BiTe and Bi$_4$Se$_3$, which are composite WTI, WTI plus TCI and TSM, respectively (figure 13(b)) [40, 57, 58]. The group of Bi
bilateral and Bi2TeX can be Bi2TeX, which is a composite
2
WTI plus TCI [43, 59]. In addition, the topological prop-
erties of other compounds, Bi1TeX and Bi2Te3, remain in-
conclusive (figure 13(c)) [60, 61]. Bi2rSe2Te2 can also intercalate
into the Bi2Te4 layer to form Bi2Te2xTe1+y and weaken
the interlayer magnetism interaction between the MBi2Te2
adjacent layers and to restore the intrinsic topological prop-
erties of monolayer MBi2Te4 (figure 13(d)) [62–65]. More
groups of these building blocks are expected to be fabricated
to realize novel topological properties. For example, the group
of Bi bilayers and MBi2Te4 is expected to give rise to the
quantum anomalous Hall effect due to the fact that the out-of-
plane moment in MBi2Te4 can break the time-reversal sym-
betry in Bi bilayer (QSHI) to create a more robust one-branch
edge state.

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