Topological edge states in single- and multi-layer Bi$_4$Br$_4$

Jin-Jian Zhou$^1$, Wanxiang Feng$^1$, Gui-Bin Liu$^2$ and Yugui Yao$^{1,2}$

$^1$ Institute of Physics, Chinese Academy of Sciences and Beijing National Laboratory for Condensed Matter Physics, Beijing 100190, People’s Republic of China

$^2$ School of Physics, Beijing Institute of Technology, Beijing 100081, People’s Republic of China

E-mail: ygyao@bit.edu.cn

Keywords: topological edge states, quantum spin hall insulator, two-dimensional materials, first-principles calculations

Abstract

Topological edge states at the boundary of quantum spin Hall (QSH) insulators hold great promise for dissipationless electron transport. The device application of topological edge states has several critical requirements for QSH insulator materials, e.g. a large band gap, appropriate insulating substrates, and multiple conducting channels. In this paper, based on first-principles calculations, we show that Bi$_4$Br$_4$ is a suitable candidate. Single-layer Bi$_4$Br$_4$ was recently demonstrated to be a QSH insulator with sizable gap. Here we find that, in multilayer systems, both the band gaps and low-energy electronic structures are only slightly affected by the interlayer coupling. On the intrinsic insulating substrate of bulk Bi$_4$Br$_4$, the single-layer Bi$_4$Br$_4$ preserves its topological edge states well. Moreover, at the boundary of multilayer Bi$_4$Br$_4$, the topological edge states stemming from different single-layers are weakly coupled, and can be fully decoupled by constructing a stair-stepped edge. The decoupled topological edge states are very suitable for multi-channel dissipationless transport. Our work indicates that an ideal QSH insulator can be prepared by nano-fabrication on the cleaved surface of layered Bi$_4$Br$_4$ single crystal.

1. Introduction

The hallmark of quantum spin Hall (QSH) insulators, also known as two-dimensional (2D) topological insulators, is the gapless helical edge states inside the bulk band gap [1, 2]. Along a given edge of a QSH insulator, a pair of edge states with opposite spins propagate in opposite directions, and they are topologically protected against backscattering from non-magnetic disorder. With this novel property, topological edge states show their potential for application in dissipationless transport, which has been demonstrated experimentally in HgTe/CdTe [3] and InAs/GaSb [4] quantum wells. Despite great promise, the device application of topological edge states has been hampered by the lack of suitable materials that meet several critical requirements, e.g. a large band gap for room temperature applications and multiple conducting channels for high signal-to-noise ratio.

Inspired by the discovery of graphene, 2D materials with atomic thickness have become an emerging playground for exploring novel physics. The QSH effect was first predicted in graphene [5], in which the band gap opened by spin–orbital coupling (SOC) is extremely small [6]. Subsequently, some honeycomb-like materials with heavier elements were proposed to be QSH insulators with experimental accessible gaps, such as silicene [7, 8] and the Bi(111) bilayer [9]. However, the lack of appropriate insulating substrates is another crucial issue. The QSH phase of 2D materials may be destroyed due to the interactions with substrates [10, 11]. Even if the QSH phase survives, the hybridization between the topological edge states and the substrate’s bulk states is disturbing [12, 13]. Topological edge modes of a Bi-bilayer on the surface of Bi single crystal were detected by STM recently [14], in which result edge states of certain edge type are only slightly hybridized with bulk Bi. Yet the metallic surface of bulk Bi is inadequate for edge state transport. Other newly proposed QSH insulators with sizable band gaps, such as single-layer Bi$_4$Br$_4$ [15] and transition metal dichalcogenides [16], may break this obstruction because their bulk crystals are insulators.
In this paper, based on first-principles calculations, we study the effect of interlayer coupling on the electronic structures and edge states of multilayer Bi₄Br₄. We find that the band gaps of multilayer Bi₄Br₄ hardly change as the number of layers increases, and the interlayer coupling has a small impact on the low-energy electronic structures of multilayer Bi₄Br₄, which is attributed to the special orbital character of the band edges. Therefore, the surface of bulk Bi₄Br₄ can be an intrinsic insulating substrate for single-layer Bi₄Br₄. With this substrate, the Fermi velocity of topological edge states is slightly reduced compared to the freestanding case. Moreover, at the boundary of multilayer Bi₄Br₄, the topological edge states stemming from different single-layers are weakly coupled, which can be further decoupled by constructing a stair-stepped edge. The decoupled topological edge states can serve as multiple conducting channels. Our results indicate that Bi₄Br₄ is an excellent candidate for manufacturing multi-channel dissipationless electron devices.

2. Computational methods

First-principles calculations are carried out using the projector augmented wave method [17] as implemented in the Vienna ab initio simulation package [18]. Both the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [19] and the Heyd–Scuseria–Ernzerhof hybrid functional (HSE06) [20] are used for the exchange-correlation potential. The energy cutoff of the plane-wave basis is set to 300 eV. The experimental in-plane lattice constants of bulk Bi₄Br₄ are used for the multilayer system. Due to weak van der Waals (vdW)-type interlayer coupling in Bi₄Br₄, the vdW corrections of Dion et al. [21, 22] are employed to relax the ionic positions until forces on each ion are less than 0.01 eV·Å⁻¹. In HSE06 calculations, maximally localized Wannier functions (MLWFs) [23] for the p-orbitals of Bi and Br atoms are constructed using the WANNIER90 code [24] on a 6 × 6 × 1 k-mesh. The edge electronic structures are calculated using a combination of MLWFs and surface Green’s function methods [25].

3. Result and discussion

Bi₄Br₄ has a layered structure [26, 27], as shown in figure 1(a). Within each single-layer, one Bi atomic layer is sandwiched by two Bi/Br atomic layers. The normal and mirror-reflected single-layers are stacked alternatively along the z direction, and the interactions between adjacent single-layers are of weak vdW-type. Single-layer Bi₄Br₄ has a thickness of ~7 Å. It can be regarded as a parallel arrangement of one-dimensional (1D) infinite molecule chains [figure 1(b)]. From the top view shown in figure 1(c), one can see that the single-layer structure belongs to the centered rectangular lattice, whose primitive unit cell is half the size of its conventional cell. The conventional unit cell consists of two 1D chains, and the lattice constants a and b are 13.064 Å and 4.338 Å, respectively [26].

The single-layer Bi₄Br₄ has recently been predicted to be a QSH insulator [15]. In the absence of SOC, the top of valence band (TVB), dominated by a Bi_in⁻px orbital, has odd parity under inversion symmetry, while the bottom of conduction band (BCB), dominated by a Bi_ex⁻px orbital, has even parity [15]. After turning on SOC, as shown in figure 2(a), both the orbital character and parity of the band edges are inverted at the R point due to the strong SOC of bismuth. This band inversion results in a non-trivial topological phase (ζ₂ = 1) in single-layer Bi₄Br₄.
From a single-layer to a multilayer system, the significant electronic properties may be altered by interlayer coupling, e.g., the direct to indirect band gap transition between monolayer and multilayer MoS$_2$ [28]. To study the effect of interlayer coupling on the electronic structure of Bi$_4$Br$_4$, especially for the inverted band gap, we calculate the band structures of few-layer Bi$_4$Br$_4$ using both GGA and HSE06 potentials. The calculated band gaps of Bi$_4$Br$_4$ from single-layer to bulk systems are shown in Figure 3(a). In the absence of SOC, the band gaps of HSE06 are obviously larger than those of GGA. This is because the GGA calculation usually underestimates the band gap [29]. In both GGA and HSE06 calculations, the band gap slightly decreases as the number of layers increases, and the differences in band gap are within $\sim 0.2$ eV. When SOC is turned on, the band gaps of multilayer Bi$_4$Br$_4$ are inverted in the similar way as single-layer system. The inverted band gaps are presented with negative values in Figure 3(a). The dependence of band gap on the number of layers is further reduced. For the HSE06 result, the band gap difference between single-layer and bulk systems is only within $\sim 30$ meV, which is a very small value compared to other layered materials, e.g., black phosphorus ($\sim 0.7$ eV) [30].

Apart from the band gaps, the low-energy electronic structures are also insensitive to interlayer coupling. Figure 3(b) shows the comparison between HSE06 band structures of single-layer and triple-layer Bi$_4$Br$_4$. The band features are essentially the same for both systems. Each band in single-layer Bi$_4$Br$_4$ corresponds to three
bands in triple-layer Bi$_4$Br$_4$, which are split due to interlayer coupling. As can be seen in figure 3(b), the band splitting around the Fermi-level is rather small, e.g., the band splitting of BCB (TVB) is about 40 (80) meV.

The small band splittings can be attributed to the special orbital characters of the band edges. When single-layers are stacked together to form a multilayer structure, the states dominated by orbitals with larger interlayer hopping usually have larger band splitting in multilayer systems. Obviously, the out-of-plane $p_z$ orbital has larger interlayer hopping compared to the in-plane $p_{xy}$ orbitals, and the orbitals from Bi$_{ex}$ have larger interlayer hopping compared to those from Bi$_{in}$. The band structure of single-layer Bi$_4$Br$_4$ with orbital projected characters is plotted in figure 3(c). The second valence bands are dominated by a Bi$_{ex}$-$p_z$ orbital, thus have relatively large band splitting of a few hundred meV in triple-layer system [figure 3(b)]. In contrast, the low-energy bands are dominated by the in-plane $p_{xy}$ orbitals, mainly Bi$_{in}$-$p_x$ [figure 2(a)], therefore they are less affected by the interlayer coupling.

In the weak coupling limit, the multilayer system can be regarded as a simple stacking of many isolated single-layers which have topological edge states at the boundaries. We now focus on the evolution of these topological edges states when a weak interlayer coupling is introduced, as is the case in multilayer Bi$_4$Br$_4$. The edge electronic structures and spin polarizations for single-layer, double-layer and triple-layer Bi$_4$Br$_4$ are shown in figure 4. Since the coupling between adjacent 1D chains is much weaker than the intra-chain bonding [26], atomically sharp edges along the 1D chain axis ($y$-direction) without dangling bonds can be stabilized. We construct such edges as semi-infinite systems, for which the surface Green’s functions are calculated. By extraction from the imaginary part of the surface Green’s function, the energy- and momentum-dependent edge density of states are used to analyze the edge electronic structures. For single-layer Bi$_4$Br$_4$ [figure 4(a)], single-Dirac-cone edge states linearly cross the bulk band gap. The Fermi velocity calculated by HSE06 is $\sim 6.5 \times 10^5$ m·s$^{-1}$, which is larger than the GGA result [15]. For double-layer Bi$_4$Br$_4$ [figure 4(b)], two pairs of topological edge states are weakly coupled, and a small gap of $\sim 20$ meV is opened. The gapped edge states indicate topological trivial phase in double-layer Bi$_4$Br$_4$. For triple-layer Bi$_4$Br$_4$ [figure 4(c)], three pairs of topological edge states are coupled. However, one pair of edge states crosses the band gap without gap opening, which indicates topological non-trivial phase in triple-layer Bi$_4$Br$_4$. The difference in topological phase is due to the multilayer Bi$_4$Br$_4$ with an even (odd) number of layers has even (odd) times of band inversions. The even times of band inversions result in a trivial insulator with $Z_2 = 0$, while odd times of band inversions result in a QSH insulator with $Z_2 = 1$.

Since the topological edge states are weakly coupled at the boundary of multilayer Bi$_4$Br$_4$, they can be decoupled by constructing a rough edge, such as a stair-stepped edge. We construct a two-layer Bi$_4$Br$_4$ film with a stair-stepped edge supported by bulk Bi$_4$Br$_4$ surface, as plotted schematically in figure 5(b). With a step width of $\sim 5$ nm, we calculate the edge energy spectrum of this system as shown in figure 5(a). The edge states linearly cross the bulk gap without gap-opening. Compared to the freestanding double-layer one [figure 4(b)], the
topological edge states from the two different layers are fully decoupled at the stair-stepped edge, and the two single-Dirac-cones are degenerate. Another observation is that, due to the weak interaction with substrate, the Fermi velocity of the decoupled edge states ($\sim 5.6 \times 10^5$ m·s$^{-1}$) is a little smaller than that of the free standing single-layer system [figure 4(a)]. As with the effect of interlayer coupling, the decreased Fermi velocity is also observed in the edge states of triple-layer systems.

To understand the essential physics, we develop a low-energy effective $k \cdot p$ Hamiltonian for single-layer Bi$_4$Br$_4$ by using the theory of invariants, from which the effective Hamiltonian for the topological edge states can be further derived. For the convenience to construct natural edges along the 1D chain axis, we adopt the conventional unit cell. Consequently the band edges are folded to the $\Gamma$-point, as illustrated in figure 2(c). Both the BCB and TVB are double degenerate, and the two degenerate states are related by time reversal symmetry. Since the BCB (TVB) has odd (even) parity under inversion symmetry, we can denote these four states as $|\downarrow, -\uparrow\rangle$, $(|\uparrow, +\downarrow\rangle$, $|\downarrow, +\uparrow\rangle$, $|\uparrow, -\downarrow\rangle)$. By analyzing the inversion, mirror $M_y$ and time reversal symmetry, we can write down the low-energy effective Hamiltonian using the four states as basis (in the order of $|\uparrow, +\rangle$, $|\downarrow, +\rangle$, $|\downarrow, -\rangle$, $|\uparrow, -\rangle$)

$$H_F(k) = e_0(k) + \begin{pmatrix} M(k) & A_1 k_x & 0 & A_2 k_y \\ A_1^* k_x & -M(k) & A_2 k_y & 0 \\ 0 & A_2^* k_y & M(k) & -A_1^* k_x \\ A_1^* k_y & 0 & -A_1 k_x & -M(k) \end{pmatrix}$$

where $e_0(k) = C + D_1 k_x^2 + D_2 k_y^2$, $M(k) = M_0 - B_1 k_x^2 - B_2 k_y^2$, $A_1$ and $A_2$ are complex parameters, while the others are real parameters. By fitting the energy spectrum of the Hamiltonian with the HSE06 band structure (see figure 2(b)), we can determine these parameters as following: $C = 0.0$ eV, $D_1 = 0.506$ eV·Å$^2$, $D_2 = 4.82$ eV·Å$^2$, $M_0 = 0.09$ eV, $B_1 = 3.86$ eV·Å$^2$, $B_2 = 0.0032$ eV·Å$^2$, $A_1 = -1.81 + 0.046i$ eV·Å, $A_2 = -4.15 + 0.141i$ eV·Å. The band inversion can be produced by the fact of $M_y$, $B_1$, $B_2 > 0$. The form of the $k \cdot p$ Hamiltonian is different from that of the HgTe quantum well[31], but similar to that of Bi$_2$Se$_3$[32]. In a similar way as for Bi$_2$Se$_3$, we can derive the effective Hamiltonian for the topological edge states.

$$H_{\text{edge}}(k_y) = A_2 |k_y, \sigma_x\rangle$$

With the fitted value of $A_2$, the Fermi velocity of the topological edge states is given by $v_F = |A_2|/\hbar \approx 6.3 \times 10^5$ m·s$^{-1}$, which is consistent with the HSE06 result (figure 4(a)). The Fermi velocity $v_F$ is reduced to $\sim 5.6 \times 10^5$ m·s$^{-1}$ when the single-layer system is supported by bulk Bi$_4$Br$_4$ surface (figure 5(a)). For the edge states of multilayer Bi$_4$Br$_4$, the effective Hamiltonian can be written by introducing coupling terms between edge states of different single-layers. For example, for the double-layer Bi$_4$Br$_4$, the effective Hamiltonian can be given by:

$$H_{\text{edge}}^{DL}(k_y) = v_F k_y \tau_0 \otimes \sigma_x + s \tau_0 \otimes \sigma_0 + t \tau_y \otimes \sigma_z$$

where $\tau$ denotes the Pauli matrices for the two different layers, $\sigma_0$ and $\tau_0$ are $2 \times 2$ identity matrix. $s$ and $t$ are the coupling parameters. Due to the mirror $M_y$ and time reversal symmetry, only two coupling terms are allowed.
4. Conclusion

In summary, first-principles calculations demonstrate that, in multilayer Bi$_4$Br$_4$, the interlayer coupling has little effect on the band gaps and low-energy electronic structures. When single-layer Bi$_4$Br$_4$ is supported by the surface of bulk Bi$_4$Br$_4$, its topological edge states survive well except for a slightly reduced Fermi velocity. Hence, bulk Bi$_4$Br$_4$ can be an ideal insulating substrate for this single-layer QSH system. Moreover, at the stair-stepped edge of multilayer Bi$_4$Br$_4$, the topological edge states from different single-layers are fully decoupled. Our results indicate that multiple dissipationless conducting channels can be realized by nano-fabrication on the cleaved surface of layered Bi$_4$Br$_4$ single crystal [14, 33], therefore Bi$_4$Br$_4$ is an excellent platform for manufacturing QSH-based devices.

Acknowledgments

This work was supported by the MOST Project of China (nos. 2014CB920903, 2013CB921903, 2011CBA00100), the NSF of China (nos. 11174337, 11274033, 11304014) and the SRFDPHE of China (no. 2012110110046, 20131101120052).

References

[1] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045
[2] Qi X L and Zhang S-C 2011 Rev. Mod. Phys. 83 1057
[3] König M, Wiedmann S, Brne C, Roth A, Buhmann H, Molenkamp L W, Qi X-L and Zhang S-C 2007 Science 318 766
[4] Knez I, Du R-R and Sullivan G 2011 Phys. Rev. Lett. 107 136603
[5] July 2005 Phys. Rev. Lett. 95 226801
[6] Yao Y, Ye F, Qi X-L, Zhang S-C and Fang Z 2007 Phys. Rev. B 75 041401
[7] Liu C-C, Feng W and Yao Y 2011 Phys. Rev. Lett. 107 076802
[8] Liu C-C, Jiang H and Yao Y 2011 Phys. Rev. B 84 195430
[9] Murakami S 2006 Phys. Rev. Lett. 97 236805
[10] Chen L, Li H, Peng B, Ding Z, Qiu J, Cheng P, Wu K and Meng S 2013 Phys. Rev. Lett. 110 085504
[11] Lin C-L, Arafune R, Kawahara K, Kanno M, Tsukahara N, Minamitani E, Kim Y, Kawai M and Takagi N 2013 Phys. Rev. Lett. 110 076801
[12] Hirahara T, Bihmayer G, Sakamoto Y, Yamada M, Miyazaki H, Kuroda S and Hasegawa S 2011 Phys. Rev. Lett. 107 166801
[13] Yang F et al 2012 Phys. Rev. Lett. 109 016801
[14] Drozdov I K, Alexandradinata A, Jeon S, Nadj-Perge S, Ji H, Cava R J, Andrei Bernevig B and Yazdani A 2014 Nat. Phys. 10 664
[15] Zhou J-J, Feng W, Liu C-C, Yuan S and Yao Y 2014 Nano Letters 14 4767
[16] Qin X, Liu J, Fu L and Ji J 2014 arXiv:1406.2749
[17] Blochl P E 1994 Phys. Rev. B 50 17953
[18] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[19] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[20] Heyd J, Scuseria G E and Ernzerhof M 2006 J. Chem. Phys. 124 219906
[21] Dion M, Rydberg H, Scuseria G E and Lischner J C and Lundqvist B I 2004 Phys. Rev. Lett. 92 246401
[22] Klimes J, Bowler D R and Michaelides A 2011 Phys. Rev. B 83 195131
[23] Marzari N and Vanderbilt D 1997 Phys. Rev. B 56 12847
[24] Mostofi A A, Yates J R, Lee Y-S, Souza I, Vanderbilt D and Marzari N 2008 Comput. Phys. Commun. 178 685
[25] Sancho M P L, Sancho J M L and Rubio J 1985 J. Phys. F: Met. Phys. 15 351
[26] Filatova T G, Gulin P V, Kloow L, Kulbachinskii V A, Kuznetsov A N, Klyuvin V G, Lindsjo M and Popovkin B A 2007 J. Solid State Chem. 180 1103
[27] Heyd J, Scuseria G E and Ernzerhof M 2006 J. Chem. Phys. 124 219906
[28] Dion M, Rydberg H, Scuseria G E and Lischner J C and Lundqvist B I 2004 Phys. Rev. Lett. 92 246401
[29] Klimes J, Bowler D R and Michaelides A 2011 Phys. Rev. B 83 195131
[30] Marzari N and Vanderbilt D 1997 Phys. Rev. B 56 12847
[31] Mostofi A A, Yates J R, Lee Y-S, Souza I, Vanderbilt D and Marzari N 2008 Comput. Phys. Commun. 178 685
[32] Sancho M P L, Sancho J M L and Rubio J 1985 J. Phys. F: Met. Phys. 15 351
[33] Filatova T G, Gulin P V, Kloow L, Kulbachinskii V A, Kuznetsov A N, Klyuvin V G, Lindsjo M and Popovkin B A 2007 J. Solid State Chem. 180 1103
[34] Heyd J, Peralta I, E, Scuseria G E and Martin R L 2005 J. Chem. Phys. 122 174101
[35] Liu H, Neal A T, Zhu Z, Luo Z, Xu X, Tommek D and Ye P D 2014 ACS Nano 8 4033
[36] Bernevig B A, Hughes T L and Zhang S-C 2006 Science 314 1757
[37] Zhang H, Liu C-X, Qi X-L, Dai X, Fang Z and Zhang S-C 2009 Nat. Phys. 5 438
[38] Sabater C, Gosalbez-Martinez D, Fernandez-Rossier J, Rodrigo J G, Utriedt C and Palacios J J 2013 Phys. Rev. Lett. 110 176802