Observation of Single Dirac Cone Topological Surface State in Compounds TlBiTe$_2$ and TlBiSe$_2$ from a New Topological Insulator Family

Yulin Chen,$^{1,2,3}$ Zhongkai Liu,$^{1,2}$ James G. Analytis,$^{1,2}$ Jiunn-Haw Chu,$^{1,2}$ Haijun Zhang,$^{1,2}$ Sung-Kwan Mo,$^3$ Robert G. Moore,$^1$ Donghui Lu,$^{1,2}$ Ian Fisher,$^{1,2}$ Shoucheng Zhang,$^{1,2}$ Zahid Hussain,$^3$ and Z.-X. Shen$^{1,2}$

$^1$Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025
$^2$Geballe Laboratory for Advanced Materials, Departments of Physics and Applied Physics, Stanford University, Stanford, California 94305
$^3$Advanced Light Source, Lawrence Berkeley National Laboratory Berkeley California, 94720, USA (Dated: June 22, 2010)

Angle resolved photoemission spectroscopy (ARPES) studies were performed on two compounds (TlBiTe$_2$ and TlBiSe$_2$) from a recently proposed three dimensional topological insulator family in Thallium-based III-V-VI$_2$ ternary chalcogenides. For both materials, we show that the electronic band structures are in broad agreement with the $ab$ initio calculations; by surveying over the entire surface Brillouin zone (BZ), we demonstrate that there is a single Dirac cone reside at the center of BZ, indicating its topological non-triviality. For TlBiSe$_2$, the observed Dirac point resides at the top of the bulk valence band, making it a large gap ($\geq$200meV) topological insulator; while for TlBiTe$_2$, we found there exist a negative indirect gap between the bulk conduction band at $M$ point and the bulk valence band near $\Gamma$, making it a semi-metal at proper doping. Interestingly, the unique band structures of TlBiTe$_2$ we observed further suggest TlBiTe$_2$ may be a candidate for topological superconductors.

PACS numbers: 71.18.+y, 71.20.-b, 73.20.-At, 73.23.-b

Topological insulators represent a new state of quantum matter with a bulk gap and odd number of relativistic Dirac fermions on the surface [1]. Since the discovery of two dimensional (2D) topological insulator in HgTe quantum well [2] and subsequent in three dimensional (3D) materials (especially the single Dirac cone family Bi$_2$Te$_3$, Bi$_2$Se$_3$ and Sb$_2$Te$_3$) [3-6], topological insulators has grown as one of the most intensively studied fields in condensed matter physics [1-11]. The massless Dirac fermions and the magnetism further link the topological insulators to relativity and high energy physics [12].

The fast development of the topological insulators also inspires the study of other topological states such as topological superconductors [13-19], which has a pairing gap in the bulk and topologically protected surface state consisting of Majorana fermions [13]. Unlike Dirac fermions in topological insulators that can have the form of particles or holes, Majorana fermions are their own antiparticles [20]. The simplest 3D topological superconductor consists of a single Majorana cone on the surface, containing half the degree of freedom of the Dirac surface state of a single cone 3D topological insulator. This fractionalization of the degree of freedom introduces quantum non-locality and is essential to the topological quantum computing based on Majorana fermions [21].

In this work, we use ARPES to study the electronic structure of TlBiTe$_2$ and TlBiSe$_2$ from a recently proposed topological insulator family: Thallium-based III-V-VI$_2$ ternary chalcogenides [22, 23]. Remarkably, both the surface and bulk electronic structures are in broad agreement with the $ab$ initio calculations; and a single Dirac cone centered at the $\Gamma$ point of surface Brillouin zone is found in both materials. Furthermore, for the p-type TlBiTe$_2$, the experimental band structure shows six leaf-like bulk valence band pockets around the Dirac cone. Given that these leaf-like bulk pockets are the only structure other than the surface Dirac cone on the Fermi-surface (FS), they may provide a possible origin of the reported bulk superconductivity [24], which can further induce superconductivity on the surface state by proximity effect, making TlBiTe$_2$ a candidate for 3D topological superconductors. Another compound of the family, TlBiSe$_2$ has a simpler bulk structure around the single Dirac cone at the $\Gamma$ point, with the Dirac point resides on top of the the bulk energy gap ($\sim$200meV), making it a large gap topological insulator similar to Bi$_2$Se$_3$ [4], but with better mechanical properties than the Bi$_2$Se$_3$/Bi$_2$Te$_3$ family, as the bonding between layers are much stronger [22] than the van de Waals’ force that bonds quintuple layer units of Bi$_2$Te$_3$ or Bi$_2$Se$_3$ [4].

The crystal structure of Thallium based III-V-VI$_2$ ternary chalcogenides is rhombohedra with the space group R-3m, which can be viewed as a distorted NaCl structure with four atoms in the primitive unit cell. A conventional unit cell of TlBiTe$_2$ is shown in Fig. 1(a) as an example: the three different types of atoms stack in layers with repeating sequence ...-Te-Bi-Te-Tl-... [25]. The existence of a flat cleavage plane [26] parallel to the (111) surface in this family of compounds [inset of Fig. 1(b)] makes them suitable for ARPES study. The high quality of the crystal was demonstrated by the XRD [Fig. 1(b)] and Laue [Fig 1(c)] characterizations; and the
The contribution of the FS evolves from an n-type pocket in the FS geometries [Fig. 2(d)]. From region I to III, the bulk nature into four regions [Fig. 2(c)] for discussion of different positions of the bulk band, we can divide the band structure into six p-type leaf-like pockets outside (Region III), with the bulk pockets disappear in region II; while in region IV, both the FS at the center and the surrounding leaf-like pockets are p-type. Fig. 2(e) shows a summary of the band evolution through all four regions.

Besides having the single Dirac cone on the surface, TlBiTe$_2$ was also reported to superconduct when p-doped [24], with $E_F$ of the corresponding density ($\sim 6 \times 10^{20}/cm^3$) resides in region III (about 150meV below the bottom of BVB). From our measurements, the FS geometry in this region is characterized by a ring like SSB FS and six surrounding p-type bulk pockets [Fig. 3(a)], as clearly shown in Fig. 2(d) - where a broad scan in $k$-space that covers four BZs [Fig. 3(b)] confirms that the FS structure in Fig. 3(a) is the only feature within each BZ. This leads to the natural conclusion that the bulk superconductivity of p-type TlBiTe$_2$ originates from the six leaf-like bulk pockets; and in the superconducting state, the surface state [the center FS pocket in Fig. 3(a,b)] can become superconducting due to the proximity effect induced by the bulk states. For such a superconductor, it has been proposed [13] that each vortex line has two Majorana zero modes related by the time reversal symmetry, thus making it a candidate for topological superconductors and suitable for the topological quantum computation [21]. However, the presence of superconductivity in p-type TlBiTe$_2$ requires further confirmation [27, 28].

The band structures of TlBiTe$_2$ in larger energy and momentum scale are shown in Fig. 3(c), where the measured dispersions (left sub-panels) along both $\Gamma - M - \Gamma$ and $\Gamma - K - \Gamma$ directions are compared with the corresponding $ab$ initio calculation of the bulk band (right sub-panels). In general, the experimental dispersions along both directions agree well with the calculation, which reproduces each bulk feature of the measurement [Fig. 3(c)], albeit the relative energy position is slightly different. Again, the non-existence of the linear dispersion of the Dirac cone in the $ab$ initio bulk calculation confirms its surface nature.

Interestingly, from the measurements [Fig. 3(c), top left panel], we find there is a small energy overlap ($\sim 20$meV) between the bottom of the electron pocket at M (BCB2) and the top of the valence band around $\Gamma$ (BVB1), indicating that TlBiTe$_2$ is a semi-metal if $E_F$ resides in this region. Also, unlike the p-type sample, the FS of an n-type TlBiTe$_2$ (electron density $\sim 10^{19}/cm^3$) shows an electron pocket at the M point [Fig. 3(d)] due to the bulk conduction band (BCB2) at the zone boundary [Fig. 3(c), top row].

The band structure of TlBiSe$_2$, another compound from the Tl-based ternary family, is summarized in Fig. 4. Similar to TlBiTe$_2$, there exists a single surface Dirac cone at the $\Gamma$ point [Fig. 4(a-f)], confirming that its topological non-triviality. The main difference between TlBiSe$_2$ and TlBiTe$_2$ is that the Dirac point of TlBiSe$_2$
resides at the top of the BVB [Fig. 4(a,b)], and the system has a $\sim 200 \text{meV}$ direct bulk gap at $\Gamma$. The bulk band structure is also simpler around $\Gamma$ and less anisotropic along $\Gamma$-$M$ and $\Gamma$-$K$ directions [Fig. 4(a,b)]. This simplicity is also shown in the constant energy contour plots [Fig. 4(c)] and its evolution [Fig. 4(d)]. Comparing Fig. 4(c) and Fig. 2(b), we notice that the SSB FS of TlBiSe$_2$ is a convex hexagon, contrast to that of TlBiTe$_2$ which shows slightly concave geometry. This difference resembles the difference between the SSB FSs of Bi$_2$Te$_3$ and Bi$_2$Se$_3$, and can be reflected by different observations in experiments such as scanning tunneling microscopy/spectroscopy STM/STS [29, 30].

Besides the simpler band geometry around $\Gamma$, the broad range FS map [Fig. 4(e)] of n-type TlBiSe$_2$ is also simpler than that of the TlBiTe$_2$ [Fig. 3(d)], without the electron pocket at the M point. This simplicity can also be seen in the band dispersions in Fig. 4(f), where although the experimental (left sub-panels) and calculated (right sub-panels) bulk band structure again show agreement in general, the BCB2 feature at M in the calculation (top right panel) was not seen in the measurements (top left panel), causing the missing of an electron pocket at M in Fig. 4e.

Acknowledgements We thank X. L. Qi, B.H. Yan and C.X. Liu for insightful discussions. This work is supported by the Department of Energy, Office of Basic Energy Science under contract DE-AC02-76SF00515.
FIG. 4: (Color) (a) 3D illustration of the band structure around Γ, with the BCB, BVB, SSB and the Dirac point indicated. (b) Detailed band structure along M-Γ-K direction, with less anisotropy compared to Fig. 2(c). The bottom of the BCB at Γ is about 100meV below $E_F$ and the Dirac point, residing on top of the BVB, is about 200meV below the BCB bottom. (c) Constant energy contours of the band structure at different binding energies. (d) Stacking constant energy plots shows the evolution of the band structure. Red dashed line traces the dispersion of the SSB from the Dirac point. (e) Broad FS map of n-type TlBiSe$_2$ shows a FS sheet without BCB pocket at M point. (f) Comparison between the measured band structure (left sub panels) and calculations (right sub-panels). Results of Γ - M - Γ (Γ - K - Γ) direction are shown on the top (bottom) row. Prominent BCB, BVB and SSB features are marked in both the measured and calculated band structures.

[1] X. L. Qi and S. C. Zhang, Phys. Today 63, 33 (2010)
[2] A. Bernevig, T. L. Hughes and S. C. Zhang, Science 314, 1757 (2006)
[3] M. Konig et al., Science 318, 766 (2007)
[4] H. Zhang, et al., Nature Phys. 5, 438 (2009)
[5] Y. Xia, et al., Nature Phys. 5, 398 (2009)
[6] Y. L. Chen, et al., Science 325 178 (2009)
[7] L. Fu, C. L. Kane and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007)
[8] X. L. Qi, T. L. Hughes and S. C. Zhang, Phys. Rev. B 78, 195424 (2008)
[9] A. P. Schnyder, S. Ryu, A. Furusaki and A. W. W. Lugwig, Phys. Rev. B 78, 195125 (2008).
[10] R. Roy, Phys. Rev. B 79, 195321 (2009)
[11] B. Seradjeh, J. E. Moore and M. Franz, Phys. Rev. Lett. 103, 066402 (2009)
[12] F. Wilczek, Nature, 458, 129 (2009)
[13] X. L. Qi, T. L. Hughes, S. Raghu and S. C. Zhang, Phys. Rev. Lett. 102, 187001 (2009)
[14] X. L. Qi, T. L. Hughes, and S. C. Zhang, Phys. Rev. B 81, 134508 (2010).
[15] A. P. Schnyder, S. Ryu, A. Furusaki and A. W. W. Lugwig, Phys. Rev. B 78, 195125 (2008).
[16] R. Roy, [http://arxiv.org/abs/0803.2685] (2008)
[17] M. Konig et al., Science 318, 766 (2007).
[18] Y. Xia, et al., Nature Phys. 5, 398 (2009)
[19] Y. S. Hor, J. G. Checkelsky, D. Qu, N. P. Ong and R. J. Cava, [http://arxiv.org/abs/1006.3017] (2010)
[20] F. Wilczek, Nature Phys. 5, 614-618 (2009).
[21] C. Nayak, S. H. Simon, A. Stern, M. Freedman and S. D. Sarma, Rev. Mod. Phys. 80, 1083 (2008).
[22] B. Yan, et. al., Euro. Phys. Lett. 90 37002 (2010)
[23] H. Lin, et. al., [http://arxiv.org/abs/1003.2615] (2009)
[24] R. Hein and E. Swiggard, Phys. Rev. Lett. 24, 53-55 (1970).
[25] F. Wilczek, Nature Phys. 5, 614-618 (2009).
[26] B. Seradjeh, J. E. Moore and M. Franz, Phys. Rev. Lett. 103, 066402 (2009)
[27] J. D. Jensen, J. R. Bruce, D. W. Ernst and R. S. Allgaier, Phys. Rev. B, 6, 319 (1972)
[28] N. S. Popovych, V. K. Shura, V. P. Daikov, I. M. Fita and G. G. Levchenko, Sol. Stat. Comm. 50, 979 (1984)
[29] L. Fu, Phys. Rev. Lett. 103 266801 (2009).
[30] Z. Alpichshev et al., Phys. Rev. Lett. 104 016410 (2010)