Experimental verification of PbBi$_2$Te$_4$ as a 3D topological insulator

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The first experimental evidence is presented of the topological insulator state in PbBi$_2$Te$_4$. A single surface Dirac cone is observed by angle-resolved photoemission spectroscopy (ARPES) with synchrotron radiation. Topological invariants $Z_2$ are calculated from the $ab initio$ band structure to be $1$; (111). The observed two-dimensional iso-energy contours in the bulk energy gap are found to be the largest among the known three-dimensional topological insulators. This opens a pathway to achieving a sufficiently large spin current density in future spintronic devices.

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Topological insulators (TI) have recently emerged as a new state of quantum matter, which are distinguished from conventional insulators by having a surface state with a massless Dirac dispersion in the bulk energy gap. The spin orientation of the topological surface state is locked with its crystal momentum, resulting in a helical spin texture. This new state can be classified by so-called $Z_2$ topological invariants\cite{1, 2}. Generally, the massless Dirac cone can be created at an interface of two materials: a topological and an ordinary insulator. The unique properties of topological surface electrons provide a fertile ground to realize new electronic phenomena, such as a magnetic monopole arising from the topological magneto-electric effect and Majorana fermions at the interface with a superconductor\cite{3, 4}. Owing to time-reversal symmetry, topological surface states are protected from backscattering in the presence of a weak perturbation, which is required for the realization of dissipationless spin transport without external magnetic fields in novel quantum devices\cite{3, 4}.

A number of materials that hold spin-polarized surface Dirac cones have been intensively studied, such as Bi$_{1-x}$Sb$_x$\cite{5, 6}, Bi$_2$Te$_3$\cite{7, 8}, Bi$_2$Se$_3$\cite{9, 10}, and thallium-based compounds\cite{11, 12}. Among them, Bi$_2$Se$_3$ has been regarded as one of the most promising candidates for potential applications in ultra-low power consumption quantum devices that can work stably at room temperature due to a sufficiently large bulk energy gap. Although significant efforts have been made towards spintronic applications, the surface contribution to conduction was hardly observed even at low bulk carrier density\cite{22, 24}. This motivates the search of new topological insulators with higher density of spin-polarized Dirac fermions.

Recently, some of the Pb-based ternary chalcogenides have been proposed as 3D topological insulators\cite{25, 27}. The present study is focused on PbBi$_2$Te$_4$, which has the simplest crystal structure among them. The crystal is composed of seven-layer blocks with the atomic layer sequence Te-Bi-Te-Pb-Te-Bi-Te [see Fig. S1(a) of supplementary material (SM)]\cite{28}. The theoretical analysis of Ref.\cite{27} indicates that this compound is a three-dimensional (3D) topological insulator. In this Letter, we report the first experimental evidence of the topological surface state in PbBi$_2$Te$_4$ by angle-resolved photoemission spectroscopy (ARPES). We establish that the size of the two-dimensional iso-energy contour, which is proportional to the surface carrier density, is the largest among the known 3D topological insulators. Thus, PbBi$_2$Te$_4$ can be counted as one of the most promising candidates for realizing a large spin current density in future spintronic devices.

A single crystalline sample of PbBi$_2$Te$_4$ was grown by the standard procedure using Bridgman method [see SM for more details]. For ARPES measurement the samples were in situ cleaved along the basal plane. Photoemission experiment was performed with synchrotron radiation at the linear undulator beamline (BL1) and the
helical undulator beamline (BL9A) of Hiroshima Synchrotron Radiation Center (HiSOR). The ARPES spectra were acquired with a hemispherical photoelectron analyzer (VG-SCIENTA R4000) at 17 K. The overall energy and angular resolutions were set to 10–20 meV and 0.3°, respectively.

Figure 1(a) shows the ARPES energy dispersion curve along the ΓK line of the surface Brillouin zone [see SM, Fig. S1(b)] measured at $\hbar \nu = 7.5$ eV. The parabolic band with the energy minimum at the binding energy of $E_B = 200$ meV is seen to exhibit a rather strong photoemission intensity near the Γ point. The position of the energy minimum does not change with the photon energy [see SM, Figs. S2(a) and S2(b)], which confirms the two-dimensional nature of this electronic state. More importantly, a linearly dispersing feature, i.e. the Dirac cone with the crossing point at $E_B = 470$ meV is observed.

Figures 1(b) and 1(c) summarize the constant energy contours (i) and their second derivatives (ii) in the $k_\parallel$ range $-0.3 \, \text{Å}^{-1} \leq k_x, k_y \leq +0.3 \, \text{Å}^{-1}$ from $E_B = 470$ meV (Dirac point) to 0 (Fermi level). The three-fold symmetrization procedure is applied only for the second derivative images. (c) Three dimensional map for $h\nu = 10$ eV.

In going away from the Dirac point, the sole hexagonally shaped contour is observed down to $E_B = 290$ meV and at smaller binding energies another state becomes enclosed inside the Dirac cone (starting with $E_B = 260$ meV). It is interpreted as the onset of the bulk conduction band (BCB) because the shape of the inner contours considerably depends on the photon energy, see Figs. 1(b) and 1(c). Below $E_B = 160$ meV the Dirac cone further deforms and practically merges into the bulk conduction band. In the map measured with $h\nu = 10$ eV the Dirac cone encloses two large and one small triangular shaped surfaces centered at Γ. At $h\nu = 7.5$ eV the shape of the inner Fermi surfaces strongly changes and becomes very complicated, which is consistent with a bulk state [see Fig. S4 of SM]. The size of the energy gap is estimated as 230 meV as shown in the 3D map for $h\nu = 10$ eV [Fig. 1(d)]. Such a large energy gap is beneficial for a high stability of the spin current conductance at room temperature.

Next we discuss the surface Dirac cone of PbBi$_2$Te$_4$ in more detail by comparing it with other 3D TIs. The Dirac cone dispersion along ΓM and ΓK is shown in Fig. 2(a) for PbBi$_2$Te$_4$ and for the well studied TIs Bi$_2$Se$_3$ and TlBiSe$_2$. Close to $E_F$ the Dirac cone energy dispersion in PbBi$_2$Te$_4$ is as steep as in the other materi-
In PbBi, but it is apparently less steep near the Dirac point.

In principle, three-dimensional materials with inversion symmetry are classified with four topological invariants $\nu_0; (\nu_1 \nu_2 \nu_3)$, which can be determined by the parity $\xi_m(\Gamma_i)$ of occupied bands at eight time-reversal invariant momenta (TRIM) $\Gamma_i=(n_1b_1+n_2b_2+n_3b_3)/2$, where $b_1$, $b_2$, $b_3$ are primitive reciprocal lattice vectors, and $n_j = 0$ or 1. The $Z_2$ invariants are determined by the equations $(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i$ and $(-1)^{\nu_k} = \prod_{n_k=1;n_k\neq 0} \delta_{i=(n_1,n_2,n_3)}$, where $\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i)$ [2]. For rhombohedral lattice of PbBi$_2$Te$_4$ the TRIMs are $\Gamma$, $Z$, and three equivalent $L$ as well as $F$ points [see SM, Fig. S1(b)]. The previous study confirmed that this compound is a strong topological insulator with the principal topological invariant $\nu_0 = 1$ [27]. Here we analyze the $(\nu_1 \nu_2 \nu_3)$ invariants. Interestingly, the parity inversion of bulk bands occurs at the $Z$ point for PbBi$_2$Te$_4$ [Fig. 3(a)], which leads to $Z_2$ invariant 1 (111). This is in contrast to the case of binary chalcogenides Bi$_2$X$_4$ (X=Se, Te), where the parity inversion takes place at the $\Gamma$ point with $Z_2$ invariant 1; (000) [3]. Note that PbBi$_2$Te$_4$ is the first case among the experimentally established topological insulators with $Z_2$ invariant 1; (111) possessing a single Dirac cone surface state. It is, thus, distinguished from the Bi$_{1-x}$Sb$_x$ alloy with the same $Z_2$ invariant [31] but with 5 or 3 pairs of surface states crossing the Fermi energy $E_F$ [5]. In Bi$_{1-x}$Sb$_x$, owing to nonzero invariants $(\nu_1 \nu_2 \nu_3)$, a one-dimensional (1D) topologically protected state can exist at the dislocation core [32]. In the case of the layered crystal the bulk dislocations can hardly exist, but other types of 1D TI states, such as edge states in thin films or 1D states at step edges are possible.
Finally, we compare the experimental ARPES results with the theoretical band structures, see Fig. 3(b). The calculated band structure well reproduces the bulk conduction band minimum located at $\Gamma$ point at 200 meV above the Dirac point. Although the bulk valence band maximum is higher in theory than in experiment, the theory well reproduces its location in k-space, that is, it appears around 1/3GM ($k|| \sim 0.3 \AA^{-1}$). Anisotropic features along different symmetry lines can be recognized above 100 meV relative to the Dirac point, as depicted in the inset. In addition, the parabolic surface state appears at $\sim 280$ meV above the Dirac point in the conduction band gap, which is consistent with the present observation [see SM, Fig.S3].

Our conclusion led by the present experiment is twofold: (i) PbBi$_2$Te$_4$ is proved to be a three-dimensional topological insulator with the energy gap of 230 meV and a single Dirac cone at the $\Gamma$ point. (ii) The size of the Fermi surface contour in the bulk energy gap is significantly larger than in the other presently known 3D topological insulators, whereby the highest carrier density of the known topological surface states is achieved. These novel findings pave a way for the efficient control of the group velocity with sufficiently large spin current density by tuning the chemical potential in the bulk energy gap.

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