Observation of a highly spin-polarized topological surface state in GeBi$_2$Te$_4$


1Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
2Hiroshima Synchrotron Radiation Center, Hiroshima University, 2-313 Kagamiyama, Higashi-Hiroshima 739-0046, Japan
3General and Inorganic Chemistry Department, Baku State University, AZ1148 Baku, Azerbaijan
4Institute of Physics, Azerbaijan National Academy of Science, AZ1143 Baku, Azerbaijan
5Laboratory of Nanostructured Surfaces and Covers, Tomsk State University, 634050 Tomsk, Russia
6Departamento de Física de Materiales UPV/EHU, Centro de Física de Materiales CEFM, and Centro Mixto CSIC-UPV/EHU, 20080 San Sebastián/Donostia, Basque Country, Spain
7Donostia International Physics Center, 20018 San Sebastián/Donostia, Basque Country, Spain

Spin polarization of a topological surface state for GeBi$_2$Te$_4$, the newly discovered three-dimensional topological insulator, has been studied by means of state-of-the-art spin- and angle-resolved photoemission spectroscopy. It has been revealed that the disorder in the crystal has a minor effect on the surface-state spin polarization, which is 70% near the Dirac point in the bulk energy gap region (~180 meV). This finding promises not only to realize a highly spin-polarized surface-isolated transport but also to add functionality to its thermoelectric and thermomagnetic properties.

DOI: 10.1103/PhysRevB.86.195304

I. INTRODUCTION

Topological insulators (TIs) have recently emerged as a new state of quantum matter and are distinguished from conventional insulators by a massless Dirac cone surface state in the bulk energy gap, the so-called topological surface state (TSS). The spin orientation of the TSS is locked with respect to crystal surface momentum, resulting in a helical state in the bulk energy gap, the so-called topological surface state. New state of quantum matter and are distinguished from conventional insulators by a massless Dirac cone surface state.

Among these materials, Bi$_2$Se$_3$ has been resolved photoemission spectroscopy (ARPES) experiment. It has been revealed that the disorder in the crystal has a minor effect on the surface-state spin polarization, which is 70% near the Dirac point in the bulk energy gap region (~180 meV). This finding promises not only to realize a highly spin-polarized surface-isolated transport but also to add functionality to its thermoelectric and thermomagnetic properties.

The crystal structure of GeBi$_2$Te$_4$ assumed in the calculation was composed of seven-layer (7L) blocks formed by the atomic layer sequence Te-Bi-Te-Ge-Te-Bi-Te, as shown in Fig. 1(a). However, the structure in the real material was found to deviate from the ideal one. It was revealed by an x-ray diffraction study that the central cation layer of the 7L block is not pure Ge but contains equal amounts of randomly distributed Ge and Bi atoms, and the other two cation layers result also in a substantial intermixing [Fig. 1(b)]. This observation prompts the important question of how the spin polarization of the TSS would be affected by the intermixing in the GeBi$_2$Te$_4$ crystal.

II. EXPERIMENT

A single crystalline ingot of GeBi$_2$Te$_4$ was grown by the vertical Bridgman-Stockbarger method. The grown crystal was characterized by x-ray diffraction using a Bruker D8 ADVANCE diffractometer with Cu $K_a$ radiation. Spin-integrated ARPES measurement was carried out with synchrotron radiation at the linear undulator beam line (BL-1) of
FIG. 1. (Color online) (a) Ideal and (b) experimentally det-

the Hiroshima Synchrotron Radiation Center (HiSOR). The
spin-resolved ARPES (SARPES) experiment was performed
with a He discharge lamp ($h\nu = 21.22$ eV) at the Efficient
SPin REsolved SpectroScoppy (ESPRESSO) end station with
the very-low-energy-electron-diffraction (VLEED)-type spin
polarimeter. The spin polarimeter utilizes [Fig. 1(d)] a
magnetic target of a Fe(001)-$p$(1×1)-O film grown on a
MgO(001) substrate, which achieves a 100 times higher
efficiency compared to those of conventional Mott-type spin
detectors. Photoelectron spin polarizations were measured
by switching the direction of in-plane target magnetizations.
This simultaneously eliminated any instrumental asymmetry,
which is a great advantage for the quantitative spin analysis
of nonmagnetic systems, as in the present case. The angle of
light incidence was 50° relative to the lens axis of the electron
analyzer. The sign of the polar (tilt) angle is defined as positive
in the case of a clockwise (anticlockwise) rotation about
$y$ axis ($x$ axis), as shown in Fig. 1(d). The energy and wave-number
resolutions for the synchrotron radiation ARPES (BL-1)
were set to better than 48 meV and 0.05 Å$^{-1}$, respectively,
while those for the ARPES (SARPES) with a He discharge
lamp were set to 19 meV and $<0.036$ Å$^{-1}$ (27 meV and
$<0.06$ Å$^{-1}$). The measurement temperatures at BL-1 and at the
ESPRESSO end station were 10 and 50 K, respectively. The
samples were cleaved in situ under an ultrahigh vacuum below
$1 \times 10^{-8}$ Pa.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the ARPES energy dispersion
curves along the $\Gamma\bar{M}$ and $\bar{K}\bar{R}$ lines of the surface Brillouin
zone (SBZ) [Fig. 1(c)], respectively. Two surface energy
bands, i.e., a TSS with a crossing point at a binding energy
$E_B$ of 260 meV (Dirac point), are clearly seen along these
lines. The bulk conduction band (BCB) is enclosed by the
TSS and crosses the Fermi energy $E_F$ with a substantial
photoemission intensity. This feature is a little different from
what is observed in the former ARPES study on the same
material, which might be due to a slight difference in
the degree of intermixing effect. The reasons for the $n$-type
conductivity of this compound are discussed and ascribed to
the predominance of the substitutional Bi$\text{Ge}$ defects, favored
by the existence of mixed cation layers in their structures,
or to $V_{\text{Te}}$ anion vacancies. Constant energy contours in the
$k_f$ range $-0.25$ Å$^{-1} \leq k_x, k_y \leq +0.25$ Å$^{-1}$ from $-200$ to
$+250$ meV with respect to the Dirac point ($E_B = 260$ meV)
are shown in Fig. 2(c). A hexagonally shaped constant energy
contour is observed at $E_F$, whose shape is preserved even at
$E_B = 150$ meV. The hexagon of the TSS evolves into the
pointlike feature at the Dirac point and is again strongly
deformed into a snowflake below the Dirac point. Another
triangular feature is enclosed within the TSS at $E_F$, which
comes from the bulk conduction band. These features are
consistent with the previous ARPES experiment. Here it has
to be mentioned that the size of the constant energy contour of
GeBi$_2$Te$_4$ ($|k_f| \sim 0.1$ Å$^{-1}$ at 150 meV above the Dirac point)
is almost twice that of the ordered Bi$_2$Se$_3$ ($\sim 0.05$ Å$^{-1}$ at
the same energy). This result implies that the intermixing of the
GeBi$_2$Te$_4$ crystal would broaden the momentum width of
the TSS.
FIG. 3. (Color online) ARPES $E$-$k_{\parallel}$ map over a wide $k_{\parallel}$ range along the $\bar{M} \bar{Γ} \bar{M}$ line acquired at $hν =$ (a) 60, (b) 64, (c) 68, (d) 72, (e) 76, (f) 80, and (g) 84 eV. Energy distribution curves in the $E_B$ range of 0–1.4 eV sliced along the constant $k_{\parallel}$ lines at (h) 0 $\AA^{-1}$ for $hν =$ 60 eV and (i) 0.3 $\AA^{-1}$ for $hν =$ 84 eV. (j) Schematics of surface (blue and red lines) and bulk band structures (gray shaded area) of GeBi$_2$Te$_4$ figured out from the present experimental results.

To determine the $k$-space location of the bulk states with respect to the TSS, we have performed a detailed photon energy dependence study over a wide $k_{\parallel}$ range. The ARPES measurements were performed with several incident photon energies $hν$ from 60 to 84 eV to cover the whole Brillouin zone along the $k_z$ direction. Figures 3(a)–3(g) show the $E$-$k_{\parallel}$ map over a wide $k_{\parallel}$ range along the $\bar{M} \bar{Γ} \bar{M}$ line acquired at $hν =$ 60–84 eV. The surface states at the $\bar{Γ}$ points in the first ($\bar{Γ}_{1\text{st}}$) and second ($\bar{Γ}_{2\text{nd}}$) SBZs are found to be identical, which signifies a single TSS in this compound. The Dirac point energy does not change with $hν$ except for a time-dependent energy shift, as will be discussed later, while the bulk states do, which again confirms their respective two- and three-dimensional natures. At $hν =$ 60 eV, the BCB enclosed by the TSS is clearly identified. In going to higher $hν$ it gradually shifts towards $E_B$ and almost vanishes finally at $hν =$ 84 eV. The bulk valence band (BVB), on the other hand, gradually grows up and shifts to lower $E_B$ with increasing $hν$, achieving its maximum (minimum in $E_B$) at $hν =$ 84 eV.

Figures 3(h) and 3(i) show the energy distribution curves (EDCs) in the $E_B$ range of 0–1.4 eV sliced along the constant $k_{\parallel}$ lines at 0 $\AA^{-1}$ for $hν =$ 60 eV and 0.3 $\AA^{-1}$ for $hν =$ 84 eV. In Fig. 3(h), a sharp peak is observed at the Dirac point energy ($E_B =$ 300 meV), and the BCB exhibits a Fermi energy cutoff accompanying a higher $E_B$ tail. The slightly higher Dirac point energy than that observed for Fig. 2 (different set of measurements) might be due to the slightly different sample stoichiometry. Here, the BCB minimum is found at $E_B =$ 140 meV (160 meV above the Dirac point) by extrapolating the higher-energy tail to “zero” intensity with a linear function. To determine the BVB maximum, another EDC is given in Fig. 3(i) and shows a monotonic decrease in intensity with decreasing $E_B$. By applying a similar fitting procedure to that used for the BCB, the BVB maximum energy is estimated to be $E_B =$ 340 meV. Since, as is commonly observed for Bi$_2$Se$_3$, the 20 meV time-dependent energy shift to higher $E_B$ occurs at the same time as that of the TSS, one may assume that the BVB maximum is located at 20 meV below the Dirac point. Thus these results lead to the conclusion that the total energy gap between the BVB maximum and BCB minimum is 180 meV in GeBi$_2$Te$_4$.

An important finding is that the Dirac point of TSS is located inside this indirect bulk energy gap (20 meV above the BVB maximum and 160 meV below the BCB minimum), as schematically shown in Fig. 3(j).

To unveil the spin characteristics of the TSS, the SARPES experiment was carried out. Two spin-integrated energy dispersion curves measured with a He discharge lamp ($hν =$ 21.22 eV) near the $\bar{Γ}$ point in the first and the second SBZs

195304-3
are compared in Figs. 4(a) and 4(b). In Fig. 4(a), a significant overlap of the bulk conduction band intensity is recognized at the first SBZ, while the bulk-derived spectral intensity is well suppressed at the second SBZ, as can also be seen in Fig. 4(b). It is apparent that it would be better to choose the second SBZ with larger emission angles for a quantitative spin analysis since the overlap of the TSS with the BCB can be avoided. Figure 4(d) shows the spin-resolved EDCs of GeBi$_2$Te$_4$ at emission angles $\theta$ of 47° (A), 53° (B), 56° (C), and 59° (D) and (e) corresponding spin polarizations. (f) ARPES results along $\Gamma M$ in the second SBZ. The contour plot has superimposed triangles pointing up and down, indicating the spin character of the corresponding spectral features, as derived from spin-resolved spectra in (d). (g) Theoretical spin-polarization values as a function of wave number obtained from the VASP first-principles calculation for ordered GeBi$_2$Te$_4$.

In conclusion, the size of the bulk energy gap for GeBi$_2$Te$_4$ is determined to be $\sim$180 meV, and topological surface state below and above the Dirac point are found to be isolated from the bulk band. Importantly, it is revealed that the disorder in the GeBi$_2$Te$_4$ crystal has a minor effect on the magnitude of the surface-state spin polarization, which shows 70% in the bulk energy gap region. This finding promises to add functionality to the already known interesting thermoelectric and thermomagnetic properties of GeBi$_2$Te$_4$. 

IV. CONCLUSION

In conclusion, the size of the bulk energy gap for GeBi$_2$Te$_4$ is determined to be $\sim$180 meV, and topological surface state below and above the Dirac point are found to be isolated from the bulk band. Importantly, it is revealed that the disorder in the GeBi$_2$Te$_4$ crystal has a minor effect on the magnitude of the surface-state spin polarization, which shows 70% in the bulk energy gap region. This finding promises to add functionality to the already known interesting thermoelectric and thermomagnetic properties of GeBi$_2$Te$_4$. 
We thank J. Jiang, H. Hayashi, Y. Nagata, and T. Horike for their technical support in the ARPES measurement at BL-1 of the Hiroshima Synchrotron Radiation Center (HSOR). This work was financially supported by Grant-in-Aid for Scientific Research Kiban A (Grant No. 23244066) and Kiban B (Grant No. 23340105) of the Japan Society for the Promotion of Science (JSPS). The ARPES measurements were performed with the approval of the Proposal Assessing Committee of HSRC (Proposal No. 12-A-24). We also acknowledge partial support from the Basque Country government, Departamento de Educaci´on, Universidades e Investigaci´on (Grant No. IT-366-07), and the Spanish Ministerio de Ciencia e Innovaci´on (Grant No. FIS2010-19609-C02-00).

ACKNOWLEDGMENTS

We thank J. Jiang, H. Hayashi, Y. Nagata, and T. Horike for their technical support in the ARPES measurement at BL-1 of the Hiroshima Synchrotron Radiation Center (HSOR). This work was financially supported by Grant-in-Aid for Scientific Research Kiban A (Grant No. 23244066) and Kiban B (Grant No. 23340105) of the Japan Society for the Promotion of Science (JSPS). The ARPES measurements were performed with the approval of the Proposal Assessing Committee of HSRC (Proposal No. 12-A-24). We also acknowledge partial support from the Basque Country government, Departamento de Educaci´on, Universidades e Investigaci´on (Grant No. IT-366-07), and the Spanish Ministerio de Ciencia e Innovaci´on (Grant No. FIS2010-19609-C02-00).