Electronic States on Bi$_2$Te$_3$ Studied by Angle-Resolved Photoelectron Spectroscopy Using Synchrotron Radiation

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We have studied the electronic structure within the topmost two quintuple layers (QL) on vacuum-cleaved n- and p-type Bi$_2$Te$_3$(111) at 10 K by angle-resolved photoelectron spectroscopy. Tunable synchrotron radiation maximized the surface sensitivity of photoelectrons. The gapless surface-state band (SSB) in the angle-resolved photoelectron spectra clearly demonstrates the topological nature of the samples. Below the SSB, the bulk valence bands (BVB) is observed. Against the three-fold symmetry of the crystal structure, the $k_z$ dispersion of the BVB is highly symmetrical around the $\Gamma$, which indicates the six-fold symmetry. Moreover, most of the BVB show almost flat $k_z$ dispersion perpendicular to the surface. These facts are the experimental evidence of a strong modification of the valence bands within the topmost two QLs into highly two-dimensional states by the advent of the surface.

Keywords: Synchrotron radiation photoelectron spectroscopy; Angle resolved photoemission; Surface electronic phenomena; Bismuth telluride; Low index single crystal surfaces; Topological insulator

I. INTRODUCTION

Bismuth telluride Bi$_2$Te$_3$ has been studied as one of the high-performance thermoelectric materials and recently as a host material of three-dimensional topological insulator by the optical and transport measurements [1–7], angle-resolved photoelectron spectroscopy (ARPES) [8–13], scanning tunneling spectroscopy [14, 15], and theoretical calculations [16–25]. Recently, Zhang et al. predicted that Bi$_2$Te$_3$ is a three-dimensional topological insulator [21] and Chen et al. experimentally demonstrated it by observing the gapless surface-state band (SSB) by ARPES [10].

As shown in Fig. 1, Bi$_2$Te$_3$ is a layered material. The primitive unit cell is a rhombohedron which contains two Bi atoms and three Te atoms [26]. The conventional hexagonal unit cell is 30.497 Å high and the edge of the basal plane is 4.386 Å long. As in Fig. 1, one Te(2) layer is sandwiched by Bi and Te(1) layers on the both side, where Te(1) and Te(2) indicate crystallographically inequivalent sites. These five atomic layers form a quintuple layer (QL) and the QLs stack in the [111] direction. The interaction between the QLs are weak van der Waals force. Therefore, Bi$_2$Te$_3$ readily cleaves between the Te(1) layers [14]. However, the interaction between the QLs must be appreciable since Bi$_2$Te$_3$ is not a two-dimensional but a three-dimensional topological insulator. Accordingly, relatively large $k_z$ dispersion perpendicular to the surface is predicted by many theoretical calculations [17–20, 23, 24], where $k_z$ is the wavevector perpendicular to Bi$_2$Te$_3$(111). Upon cleavage, the topmost QLs must be strongly perturbed by losing the interacting partner QL, and as a consequence the SSB advents and its electronic structure must be strongly modified from the bulk one. Then, the electronic structure within the topmost two QLs is particularly important because the SSB localizes within them [27]. In these terms, we have studied the electronic structure of Bi$_2$Te$_3$(111) by ARPES tuning photon energy ($h\nu$) so as to maximize the surface sensitivity. We used $h\nu$ ranging from 47.8 to 66.9 eV. At these $h\nu$, the inelastic mean free path for electrons, in other words, the escape depth of photoelectron for nearly normal emission becomes minimized to about 5 Å according to Seah and Dench [28]. This means that 98% of the observed photoelectrons from the valence-band region come from the topmost two QLS, assuming that the photoelectron intensity decreases exponentially with travelling distance. Therefore, the surface sensitivity of the present study is sufficiently high.

II. EXPERIMENTAL

A. Apparatus

All the measurements were conducted at the Saga-University beamline BL13 in Saga Light Source [29]. At BL13, synchrotron radiation, which is linearly polarized in the horizontal plane, is available from a recently upgraded planar undulator. The incident angle of the synchrotron radiation is 45°. Because the $h\nu$ from 40 to 800 eV is available, the observation of photoelectrons from not only valence bands but also shallow core levels is possible. The photon flux is in the range of $10^5$–$10^{11}$ pho-
B. Sample preparation

We grew Bi$_2$Te$_3$ single crystals in Yamagata University as in the following procedures. Commercial Bi$_2$Te$_3$ powders were melt at 900°C and then were crystallized several times followed by slow cooling with a rate of $-10$ K/h. As usual, thus obtained sample is p-doped with excess Bi substituting Te sites [1]. In order to change the carrier type, we added Te powders to the host p-type Bi$_2$Te$_3$ and melt them at 900°C again, followed by crystallization at the cooling rate of $-10$ K/h. The grown sample is indeed n-doped with excess Te substituting Bi sites.

Just before measurements, the sample was vacuum-cleared in-situ and was transferred to another UHV chamber for photoelectron spectroscopy without exposing to air. The base pressure of the analyzing chamber was $2\times10^{-8}$ Pa. The crystallinity and cleanliness were checked by low-energy electron-diffraction (LEED) patterns and photoelectron spectra taken at $h\nu = 670$ eV, respectively. Actually, very sharp LEED patterns were observed, which indicates the high quality of the cleaved Bi$_2$Te$_3$(111).

Figure 2 is the x-ray photoelectron spectrum for vacuum-cleared n-Bi$_2$Te$_3$ taken at $h\nu = 670$ eV, which shows that contaminations such as C and O are negligible whereas distinct C1s and O1s peaks are observed in the spectrum for air-cleared n-Bi$_2$Te$_3$.

III. RESULTS AND DISCUSSION

Figure 3 shows the photoemission intensity plots of p-Bi$_2$Te$_3$ along the $\bar{\Gamma}$-$\bar{M}$ direction of the surface Brillouin zone (BZ) in the angle-resolved mode taken at (a) $h\nu = 60.4$ eV (Point $\Gamma$) and (b) $66.9$ eV (Point $Z$). The sample temperature is 10 K.
to Larson et al. more asymmetrical than the present result [9]. Observed the BVB with $h\nu = 19 \text{ eV}$, which is more bulk-sensitive than our condition. Moreover, Noh et al. observed the BVB with $h\nu = 23.0 \text{ eV}$, which is still bulk-sensitive than our condition, and the observed BVB are more asymmetrical than the present result [9]. According to Larson et al. [17], the BVB have a larger Te(1) 5$p$ character than Bi 6$p$ or Te(2) 5$p$ character. At the topmost surface, therefore, originally three-fold symmetrical BVB of mainly Te(1) 5$p$ character get to have a six-fold symmetry, exhibiting the symmetrical $k_z$ dispersion around the $\bar{\Gamma}$ point. The spectra at these two $h\nu$ in Fig. 3 are very similar to each other and is in very good agreement with the spectrum at $h\nu = 47.8 \text{ eV}$ (Point $\bar{\Gamma}$) for $n$-Bi$_2$Te$_3$ (not shown). This fact indicates that the observed peaks in the spectra show no shift in energy and thus no dispersion perpendicular to the surface. This is against the fact that Bi$_2$Te$_3$ is a three-dimensional topological insulator [10] and many theoretical predictions [17–20, 23, 24]. These observations indicate a strong modification of the valence bands within the topmost two QLs into highly two-dimensional states by the advent of the surface.

Figure 5 compares the normal-emission photoelectron spectra of $n$- and $p$-type Bi$_2$Te$_3$ taken at $h\nu = 60.4 \text{ eV}$ (Point $\bar{\Gamma}$). The intensity is normalized to the maximum height. The spectrum of $p$-Bi$_2$Te$_3$ is shifted by 0.9 eV toward higher binding energy for comparison.

from the crossing point. For $p$-Bi$_2$Te$_3$, the band velocity and the Dirac point are 3.2±0.3 eVÅ (4.8×10$^5$ m/s) and 0.21±0.02 eV, respectively. From the photoelectron intensity plot of the SSB on $p$-doped Bi$_{2-x}$Mn$_x$Te$_3$ by Hsieh et al., the band velocity was estimated to be 2.9 eVÅ [12] which is in good agreement with the present result. The band velocity and the Dirac point for $n$-Bi$_2$Te$_3$ are determined to be 2.8±0.3 eVÅ (4.2×10$^5$ m/s) and 0.35±0.01 eV, evaluated also from the photoemission intensity plot taken at $h\nu = 47.8 \text{ eV}$. These values are reasonable because they are similar to 2.55 eVÅ and 0.34 eV reported for $n$-Bi$_2$Te$_3$ by Chen et al. [10]. The band velocity for $n$-Bi$_2$Te$_3$ is slightly smaller than that for $p$-Bi$_2$Te$_3$.

Figure 4(a) shows the photoemission intensity plot for the SSB of $p$-Bi$_2$Te$_3$ along the $\bar{\Gamma}$–M line in the angle-resolved mode taken at $h\nu = 60.4 \text{ eV}$. Figure 4(b) is the momentum-distribution curves (MDC) at several binding energies. The peak position in the MDCs are determined by fitting Gaussian functions. The band velocity of the SSB are evaluated from the linear fitting of thus determined peak positions and the Dirac point of the SSB.
the acceptor states of $p$-Bi$_2$Te$_3$ is almost unoccupied and therefore cannot be observed, which is the case. The other differences are found for the peaks #2, 4 and 7. These peaks for $p$-Bi$_2$Te$_3$ are slightly smaller than those for $n$-Bi$_2$Te$_3$. These peaks might originate from Te 5p and the smaller concentration of Te in p-Bi$_2$Te$_3$ might reduce the photoemission intensity.

IV. CONCLUSION

We studied the electronic structure within the topmost two QLS on vacuum-cleaved $n$- and $p$-type Bi$_2$Te$_3$(111) at 10 K by angle-resolved photoelectron spectroscopy. Tunable synchrotron radiation maximized the surface sensitivity of photoelectrons. The gapless SSB in the angle-resolved photoelectron spectra clearly demonstrates the topological nature of the samples. Below the SSB, the BVB were observed. Against the three-fold symmetry of the crystal structure, the $k$ dispersion of the BVB is highly symmetrical around the $\Gamma$, which indicate the six-fold symmetry. Moreover, most of the BVB show almost flat $k_\perp$ dispersion perpendicular to the surface. These facts are the experimental evidence of a strong modification of the valence bands within the topmost two QLS into highly two-dimensional states by the advent of the surface.

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