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 $k_{\perp}$ dispersion of the BVB is highly symmetrical around the \( \Gamma \), which indicates the six-fold symmetry. Moreover, most of the BVB show almost flat $k_{\perp}$ 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.

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 $k_{\perp}$ dispersion perpendicular to the surface is predicted by many theoretical calculations [17–20, 23, 24], where $k_{\perp}$ 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 $10^8$–$10^{11}$ photon
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 melted 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-cleaved in-situ and was transferred to another UHV chamber for photoelectron spectroscopy without exposing to air. The base pressure of the analyzing chamber was 2×10$^{-8}$ Pa. The crystallinity and cleanliness were checked by low-energy electron-diffraction (LEED) patterns and photoelectron spectra taken at $hv = 670$ eV, respectively. Actually, very sharp LEED patterns were observed, which indicates the high quality of the cleaved Bi$_2$Te$_3$. Figure 2 is the x-ray photoelectron spectrum for vacuum-cleaved n-Bi$_2$Te$_3$ taken at $hv = 670$ 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-cleaved 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) $hv = 60.4$ eV and (b) 66.9 eV. The Fermi level taken at $hv = 60.4$ eV and 66.9 eV corresponds to the $\bar{\Gamma}$ and Z points in the bulk BZ, respectively, assuming $V_0 = 10$ eV as the inner potential [8, 9, 30]. In the figure, the SSB and BVB are clearly resolved as explained below. One can see that the gapless SSB is clearly observed in the binding-energy range of 0.0-0.2 eV centered at $\bar{\Gamma}$ [10] (See Fig. 4 also). The presence of the gapless SSB is the direct experimental evidence that Bi$_2$Te$_3$ in the present paper is surely a topological insulator. Below the SSB, there are observed the SSB and BVB. Most of the BVB below $E_{\text{BVB}}$ dispersion around the $\bar{\Gamma}$ whereas others above $E_{\text{BVB}}$ is slightly asymmetrical. Here, $k_{\parallel}$ is the wavevector parallel to the surface. In Fig. 3 (b), for example, the band at 1.0 eV at the $\bar{\Gamma}$ point disperses upwards towards the $\bar{M}$ and $\bar{M}'$ points, however the dispersion to-
et al. observed the BVB with bulk-sensitive than our condition. Moreover, Noh observed the three-fold BCB with surface, therefore, originally three-fold symmetrical BVB or Te(2) 5 character than Bi 6 p.

These observations indicate a strong modification of the 2 Bi 3 dispersion around the 2-Γ point. The intensity is normalized to the maximum height.

Figure 4(a) shows the photoemission intensity plot for the SSB of 2-Bi 2Te 3 along the 2-Γ-M line in the angle-resolved mode taken at hv = 60.4 eV (Point Γ). The intensity is normalized to the maximum height. The spectrum of 2-Bi 2Te 3 is shifted by 0.9 eV toward higher binding energy for comparison.

Figure 5 compares the normal-emission photoelectron spectra of n-type 2-Bi 2Te 3 taken at hv = 60.4 eV (Point Γ). The intensity is normalized to the maximum height. The spectrum of 2-Bi 2Te 3 is shifted by 0.09 eV toward higher binding energy for comparison. The shift of the BVB and SSB by 0.09 eV is very close to that of the core levels by 0.10 eV. The shift of the BVB and SSB by 0.09 eV is smaller than the reported energy gap of 0.15 eV [3] and the direction of the shift is consistent with the p-type nature. The shift of the BVB and SSB by 0.09 eV is very close to that of the core levels by 0.10 eV. Other than the SSB, there are observed 10 peaks as numbered from zero to nine. Although the two spectra are almost identical to each other, there are some differences between the spectra of n-type 2-Bi 2Te 3. One of them is at the foot of the SSB. For n-Bi 2Te 3, the peak #0 is clearly found, however the peak is missing for p-Bi 2Te 3. We attribute the peak #0 as the impurity band as Greanya et al. [8] That is, the impurity peak #0 of n-Bi 2Te 3 is the donor states due to excess Te which are barely excited at low temperature as 10 K. On the other hand,
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 $k_{\parallel}$ 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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