Anti-site defect effect on the electronic structure of a Bi$_2$Te$_3$ topological insulator

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Tuning the Fermi level ($E_F$) in Bi$_2$Te$_3$ topological-insulator (TI) films is demonstrated on controlling the temperature of growth with molecular-beam epitaxy (MBE). Angle-resolved photoemission spectra (ARPES) reveal that $E_F$ of Bi$_2$Te$_3$ thin films shifts systematically with the growth temperature ($T_g$). The key role that a Bi-on-Te(1) (BiTe$_1$) antisite defect plays in the electronic structure is identified through extended X-ray-absorption fine-structure (EXAFS) spectra at the Bi L$_{3}$-edge. Calculations of electronic structure support the results of fitting the EXAFS, indicating that the variation of $E_F$ is due to the formation and suppression of Bi$_{Te1}$ that is tunable with the growth temperature. Our findings provide not only insight into the correlation between the defect structure and electronic properties but also a simple route to control the intrinsic topological surface states, which could be useful for applications in TI-based advanced electronic and spintronic devices.

1. Introduction

Topological insulators (TI) are novel quantum materials with promising applications in advanced spintronic devices. A three-dimensional (3D) TI is a gapped bulk insulator, but possesses gapless conducting surface states. These topological surface states in 3D TI arise from a band inversion of the valence and conduction bands due to strong spin–orbit interactions. This inversion makes the surface state topologically nontrivial, being protected by the time-reversal symmetry. The surface state in 3D TI shows a helical Dirac-type dispersion, in which the spin is tightly coupled to the momentum, so called spin-momentum locking. V$_2$-VI$_3$-type 3D TIs, such as Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$, have been theoretically predicted and experimentally confirmed. Bi$_2$Te$_3$ belongs to the V$_2$-VI$_3$ TI family and has a rhombohedral crystal structure that can be considered to consist of the stacking of -Te(1)-Bi-$Te(2)$-Bi-$Te(1)$ quintuple layers (QL). Within a QL unit, the interaction between Bi and Te is a chemical force whereas the interaction between two QL involves a van der Waals force. The surface states of Bi-based TI families are widely regarded as ideal systems for applications in spintronic and quantum devices, but a large bulk charge-carrier contribution generally originates from intrinsic defects, such as anion vacancies and antisite defects in Bi-based TI. When the charge carrier is dominated by bulk donors, the Dirac point (DP) is located deep below the Fermi level, making it difficult to utilize the unique property of the topological surface states. Understanding and manipulating the electronic structure during the growth of a thin film of TI becomes a crucial problem, especially for the effect of key parameters such as the growth temperature on the electronic structure of TI.

For a Bi$_2$Te$_3$ single crystal near the solid–liquid equilibrium composition for Te ranging from 58 to 62.8 atomic per cent, a substitution of Bi for a Te(1) site (Bi$_{Te1}$) is energetically favored and hole charge carriers dominate. In contrast, electron carriers dominate the behavior in the case of substitution of Te for Bi (Te$_{Bi}$) for Te in a range from 62.8 to 66 atomic per cent. For single-crystalline Bi$_2$Te$_3$, the p-type and n-type charge-carrier concentration can range from $3 \times 10^{17}$ to $5 \times 10^{19}$ cm$^{-3}$, depending on the initial growth condition with excess either Bi or Te. For bulk Bi$_2$Te$_3$ crystal growth near the solid–liquid
equilibrium temperature, anti-site defects can be simply described by element compositions. In comparison, thin film growth is far from the equilibrium conditions, so that the composition of Bi/Te can be tuned by growth temperature. In the present work, we report a systematic study of the crystal structure and electronic properties of epitaxial Bi₂Te₃ films upon tuning the growth temperature. A correlation between the position of the Dirac point of Bi₂Te₃ films via angle-resolved photoemission spectra (ARPES) and the coordination number of Bi–BiTe and TeBi antisite defects with density-functional theory (DFT); the results support pressure during growth was kept below 1

To remove any possible contaminant from the surface, we heated procedures before being loaded into the growth chamber. To sapphire substrates were chemically cleaned with standard vacuum (UHV) environment. Highly pure Bi (99.99%) and Te (99.999%) were evaporated from Knudsen cells; the vacuum of the MBE system was less than 2

The stoichiometry and electronic structure of the Bi₂Te₃ films were characterized with X-ray photoemission spectra (XPS) and ARPES. The XPS and ARPES experiments were conducted at beamlines 24A and 21B1 at Taiwan Light Source in National Synchrotron Radiation Research Center. The MBE-grown Bi₂Te₃ films with a Te capping layer of thickness ~20 Å were annealed at 260 °C about 1 h in an UHV environment to remove the capping layer before XPS and ARPES measurements. XPS were recorded with an energy analyzer (SPEC Phoiboss150); the core levels of Bi 4f and Te 3d were recorded with photon energy 800 eV. The incident photon energy for XPS measurements was calibrated with Au 4f levels. ARPES were recorded for samples in an UHV chamber equipped with a hemispherical analyzer (Scienz R4000, collection angle ±15°). The ARPES were recorded for samples at 83 K, base pressure 5 × 10⁻¹¹ Torr and photon energy 22 eV; the angular resolution was 0.2° and overall energy resolution was better than 12 meV. The position of the Dirac point was determined from an analysis of momentum distribution curves (MDC).

2.3 EXAFS characterization

The local structure of Bi₂Te₃ thin films was determined with EXAFS spectra. The L₃-edge spectra of Bi (13 419 eV) were recorded near 296 K at beamline 07 A of NSRRC and Taiwan beamline SP12B2 of SPring-8. The fluorescence mode was implemented with the beam incident at 54.7° with respect to the sample plane; the signal was collected with a Lytle detector. The measured energy resolution of the used double-crystal Si(111) monochromator was better than 0.6 eV.

2.4 Computational

In this work we used spin-polarized density-functional calculations as implemented in the Vienna ab initio simulation package (VASP) to derive the electronic band structure. The local-density approximation was selected for the exchange-correlation potential including spin–orbit interaction (SOI). The electron–ion interaction was represented by the projector-augmented wave potential. The cutoff energy for the expansion of wave functions and potentials in the plane-wave basis was chosen to be 300 eV. A 9 × 9 × 1 sampling of k points in the first Brillouin zone was adopted. A vacuum space in the super-cell was allocated on setting a minimum height 15 Å above the film in the cell, which was proved to be sufficient to minimize artificial interactions between supercells.

3. Results and discussion

Fig. 1 depicts the XRD pattern of the MBE-grown Bi₂Te₃ films at substrate temperature Tₛ ranging from 310 °C to 430 °C. For the films grown at lower substrate temperature of Tₛ = 310 °C, the
(015) lattice plane that can be attributed to the rhombohedral Bi$_2$Te$_3$ structure is also observed. The main feature of the XRD patterns of these Bi$_3$Te$_3$ samples is clearly close to that of Bi$_2$Te$_3$ (0001) single crystal.

ARPES were measured to probe the quality and electronic structure of MBE-grown Bi$_2$Te$_3$ films. Fig. 2 shows the band structure recorded along direction $\Gamma$–$K$. In addition to the broad M-shaped valence-band (VB) feature located at binding energy 0.3 eV, a linear band dispersion associated with the topological surface state (TSS) was clearly observed in each sample. ARPES in a series of Fig. 2(a)–(d) show that the Fermi level varied with the growth temperature, $T_g$. At $T_g = 310 \degree C$, the Dirac point is located at the binding energy ($E_D$) $= -0.320$ eV; the bottom of the conduction band appears below the Fermi level. On increasing $T_g$ to 370 $\degree C$ and 390 $\degree C$, the position of the Dirac point shifted to $E_D = -0.305$ eV and $-0.295$ eV, respectively. A similar tendency of the position variation of the Dirac point with increasing $T_g$ below 400 $\degree C$ was reported by Guang Wang et al., but when $T_g$ was further increased to 410 $\degree C$ and 430 $\degree C$, we observed an opposite trend in which the position of the Dirac point shifted further to $E_D = -0.315$ eV and $-0.335$ eV, respectively. The ARPES result shows a turning point of the position of the Dirac point that occurred at $T_g \sim 390 \degree C$. As $E_F$ was located above DP for all samples, the result indicates that the charge carriers of the Bi$_2$Te$_3$ films were dominantly n-type so that $E_F$ became tunable on varying growth temperature $T_g$.

Hole-dominated carriers with $E_F$ located within the bandgap is expected if the electronic structure were determined mainly by the antisite defects in Bi$_2$Te$_3$, but the film growth occurred far from the equilibrium growth conditions of a bulk single crystal. The formation of Te vacancies can hence not be avoided during the growth of a Bi$_2$Te$_3$ film. Te vacancies likely provide n-type carriers as the majority carriers for all Bi$_2$Te$_3$ films. It is difficult to perform quantitative analysis on the Te vacancies although they play an important role in the electronic structure. Besides point defects in Bi$_2$Te$_3$, antisite defects, substitutional Bi on Te site (Bi$_{Te}$) or substitutional Te on Bi site (Te$_{Bi}$) are energetically favored. The tendency of Fermi level shift in the Bi$_2$Te$_3$ films observed by ARPES suggests the major defects are Te vacancies and/or Bi$_{Te}$. Note that the Te vacancies acts as double donors while the Bi$_{Te}$ as triple acceptors. Therefore, n-type behavior in the Bi$_2$Te$_3$ films can be attributed to Te vacancies that donate electrons to the conduction band. This is consistent with the ARPES observation that the positions of the Fermi level are close to the conduction band. However, the ARPES data show clearly that $E_F$ varies with growth temperature $T_g$, which indicates that antisite defects also play a role in this case. According to the previous reports, a shift of the Fermi level in Bi$_2$Te$_3$ depends strongly on the native point of antisite defects (Bi$_{Te}$ and Te$_{Bi}$) in the Bi–Te compound. Near a stoichiometric Bi$_2$Te$_3$ with Te fraction about 62.8 at%, acceptor-like Bi$_{Te}$ antisite defects can dominate the carrier behavior. Donor-like Te$_{Bi}$ antisite defects are energetically favored at a larger Te composition, above 63%. The ratio of Bi and Te can be estimated qualitatively from XPS measurements with a peak analysis of the core level spectra of Bi 4f and Te 3d; the secondary electron background is removed with the Shirley background subtraction, as shown in Fig. 3(a) and (b).

The tendency that the Fermi level shifted toward the Dirac point in APRES as $T_g$ increased from 310 to 390 $\degree C$ implies that the concentration of Bi$_{Te}$ antisite defects increased with increasing $T_g$, as shown in Fig. 3(d). The highest Te fraction at 390 $\degree C$ as revealed in XPS might indicate the diffusion of Te atoms towards the outermost surface. The reduction of Te fraction at $T_g > 390 \degree C$ can be attributed to the desorption of Te from the surface. Nevertheless, a shift of $E_F$ away from the DP at $T_g > 390 \degree C$ indicates a redistribution of the Bi$_{Te}$/Te$_{Bi}$ ratio at the elevated growth temperatures. Detailed studies regarding the antisite defects dependent on growth temperature enable a quantitative analysis with EXAFS in the following.

To verify our deductions about the antisite defects, we performed Fourier transformation of the X-ray absorption spectra (XAS) at the Bi-L$_3$ edge; the radial distribution function is shown in Fig. 4(a). The fitted results of extended X-ray-absorption fine-structure (EXAFS) spectra enable a direct identification of the antisite defects in Bi$_2$Te$_3$ films. In this EXAFS work we took Bi

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**Fig. 2** Band structure of Bi$_3$Te$_3$ at various $T_g$: (a) 310 $\degree C$ (DP = $-0.32$ eV), (b) 370 $\degree C$ (DP = $-0.305$ eV), (c) 390 $\degree C$ (DP = $-0.295$ eV), (d) 410 $\degree C$ (DP = $-0.315$ eV), (e) 430 $\degree C$ (DP = $-0.335$ eV). All spectra were recorded along the $\Gamma$–$K$ direction. The panels show the ARPES intensity maps. The surface states, valence band and conduction band of the bulk states are denoted SS, VB and CB, respectively.
Fig. 3 XPS of (a) Bi-4f core-level spectra and (b) Te-3d core-level spectra of the Bi$_2$Te$_3$ thin film grown at 390 °C. (c) Total carrier concentration of the Bi$_2$Te$_3$ films as a function of the growth temperature measured by Hall measurement. (d) The Te/Bi ratio of the Bi$_2$Te$_3$ thin films as a function of the growth temperature.

Fig. 4 EXAFS spectra at the Bi L$_3$-edge of the Bi$_2$Te$_3$ thin films. The curves are vertically shifted for the substrate temperature. (a) Fourier transform of the R-space (symbols) together with the theoretical fit to the first shells [solid line]. (b) $k$-Space (symbols) together with the best fit (solid line). (c) Hexagonal conventional unit cells of Bi$_2$Te$_3$; schematic diagram of one QL of the mechanism of the antisite defect in Bi-rich and Te-rich conditions, respectively. (d) Bi$_{Te}$ antisite of Bi average coordination number and Dirac point at binding energy plotted versus $T_g$. (e) Bi$_{Te}$ antisite of Bi average coordination number and surface carrier concentration plotted versus $T_g$.

instead of Te as the central atom, because the two Te sites in each unit cell make the analysis difficult. Herein, EXAFS spectra were recorded with the background subtraction of the XAS data $\mu(E)$ and conversion of $\mu(E)$ to $\chi(k)$; both processes were performed with ATHENA using the IFEFFIT XAS package. The Fourier transforms (FT) of $k$-weighted EXAFS spectra use Hann windows with $k$ ranging from 1.2 to 10 Å$^{-1}$, as shown in Fig. 4(b). The rhombohedral primitive and hexagonal unit cell of Bi$_2$Te$_3$ consists of a five-layer lamellar structure of one quintuple layer (QL). The schematic diagram in Fig. 4(c) shows that a $-\text{Te}(1)-\text{Bi}-\text{Te}(2)-\text{Bi}-\text{Te}(1)-$ five-layer structure; one Bi atom coordinates three Te atoms at each Te site. According to calculations that provided predictions for the Bi-rich condition, Bi$_{Te}$ has the least formation energy, 0.4 eV and 0.9 eV, which is less than for Bi$_{Te1}$ and Te$_{Bi}$, respectively. For a Te-rich condition, Te$_{Bi}$ has the least formation energy, 0.7 eV and 1.1 eV, which is less than for Bi$_{Te1}$ and Bi$_{Te2}$, respectively. The coordination relevant for Bi and Te(1) and the bond length of quantitative analysis is indicated in Table 1. At growth temperatures $T_g = 310, 370$ and $390$ °C, the coordination numbers of Bi–Bi$_{Te}$ (N$_{Bi-Bi_{Te}}$) that correspond to the substitution of Bi for Te(1) are 1.05 ± 0.11, 1.312 ± 0.47 and 2.725 ± 0.35, respectively. Accordingly, the length of the Bi–Te(1) bond decreased to 3.04 ± 0.31 Å, 3.02 ± 1.07 Å, and 2.88 ± 0.37 Å, as more Te(1) sites became occupied with Bi atoms. When the growth temperature exceeded 390 °C, the coordination number of Bi–Bi$_{Te}$ (N$_{Bi-Bi_{Te}}$) decreased to 0.77 ± 0.06 at $T_g = 410$ °C. Moreover, no substitution was observed at $T_g = 430$ °C. The length of the Bi–Te(1) bond increased to 3.06 ± 0.23 Å and 3.04 ± 0.36 Å at $T_g = 410$ and 430 °C respectively.

On increasing growth temperature $T_g$ to 390 °C, the fitted results of EXAFS clearly show the substitution of a Te(1) site by a Bi atom with increased coordination number of Bi–Bi$_{Te}$. Because of the extra holes created from antisite Bi$_{Te}$, a smaller Fermi level crossing $k_F$ was observed from ARPES, indicating a decreased concentration of electron carriers. For a growth temperature above $T_g = 390$ °C, the coordination number of Bi–Bi$_{Te}$ decreased, accompanied with an incremented concentration of electron carriers as shown in Fig. 4(d). The evolution of the DP ($E_F$) as a function of growth temperature $T_g$ exhibits a trend similar to that of the coordination number of Bi–Bi$_{Te}$, as displayed in Fig. 4(e). Both the $T_g$-dependent DP and Bi–Bi$_{Te}$ coincide with the variation in the concentration of electron carriers.

Table 1 Rhombohedral primitive of first-shell EXAFS fitted results for Bi$_2$Te$_3$ TI thin films. N$_{Bi-Tel}$ is the Bi–Te(1) average coordination number, BL$_{Bi-Tel}$ is the Bi–Te(1) bond length, and N$_{Bi-Bi_{Te}}$ is the Bi$_{Te}$ antisite of Bi–Bi average coordination number, BL$_{Bi-Bi_{Te}}$ is the Bi$_{Te}$ antisite of the Bi–Bi bond length.

| Sample | $N_{Bi-Tel}$ | BL$_{Bi-Tel}$ (Å) | $N_{Bi-Bi_{Te}}$ | BL$_{Bi-Bi_{Te}}$ (Å) |
|--------|--------------|-------------------|-----------------|-------------------|
| $T_g = 310$ °C | 1.67 ± 0.17 | 3.04 ± 0.31 | 1.05 ± 0.11 | 3.13 ± 0.32 |
| $T_g = 370$ °C | 1.6 ± 0.57 | 3.02 ± 1.07 | 1.312 ± 0.47 | 3.11 ± 1.1 |
| $T_g = 390$ °C | 2.39 ± 0.31 | 2.88 ± 0.37 | 2.725 ± 0.35 | 3.11 ± 0.4 |
| $T_g = 410$ °C | 1.06 ± 0.08 | 3.06 ± 0.23 | 0.77 ± 0.06 | 3.17 ± 0.24 |
| $T_g = 430$ °C | 1.3 ± 0.16 | 3.04 ± 0.36 | None | None |
Bi-rich and Te-rich conditions further revealed that the variation of the electronic structure in Bi$_2$Te$_3$ films can be attributed to the antisite defects that are tunable with the growth temperature. Our approaches and results demonstrated the growth of homogenous n-type Bi$_2$Te$_3$ films, showing the potential for topological insulator-based device applications.

**Author contributions**

S. H. Su, C. W. Chong and J. C. A. Huang designed and prepared the experiment. P. Y. Chuang, W. C. Chen, C.-M. Cheng and K.-D. Tsuei performed ARPES measurements. The thin-film growth was performed by Y. F. Chen, Y. H. Chou, and P. Y. Chuang, for C.-H. Wang, Y. F. Liao, S. C. Weng, J. F. Lee, and Y.-W. Yang characterized samples with XPS and EXAFS. Y. K. Lan, S. L. Chang, C. H. Lee, C. K. Yang provided theoretical support. All authors have given approval to the final version of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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