The surface band structure of Bi$_{1-x}$Sb$_x$(111)

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(Dated: December 16, 2014)

Theoretical as well as experimental studies agree on Bi$_{1-x}$Sb$_x$ ($0.07 \leq x \leq 0.21$) to be a 3D topological insulator. However, there is still a debate on the corresponding Bi$_{1-x}$Sb$_x$(111) surface band structure. While experimentally three spin polarized bands have been claimed, theoretically only two surface bands appear with the third band attributed to surface imperfections. Here, we address this controversy using angle-resolved photoemission spectroscopy (ARPES) on Bi$_{1-x}$Sb$_x$ films. To minimize surface imperfections, we have optimized the sample growth recipe. We have measured the evolution of the surface band structure of Bi$_{1-x}$Sb$_x$ with $x$ increasing gradually from $x = 0$ to $x = 0.6$. Our ARPES data show a better agreement with the theoretical calculations, where the system is topologically non-trivial with two surface bands.

PACS numbers: 79.60.-i, 73.20.-At, 73.21-Fg, 75.70.-Tj

Topological insulators (TIs) are characterized by ungapped and protected edge/surface states that render the surface metallic. These states exhibit a non-trivial topology that imposes an odd number of crossings with the Fermi level [1, 2]. The first angle-resolved photoemission spectroscopy (ARPES) data showing the non-trivial topology have been measured on the (111) surface of the semiconducting phase of a Bi$_{1-x}$Sb$_x$ single crystal for $x = 0.1$ [3]. Its experimental band structure is similar to pure Bi(111) especially at the $\Gamma$-point where two spin-polarized surface bands emerge from the bulk valence band continuum [4–6]. However, the band structure around the $\overline{M}$-point is still controversial. While experimentally the topological character has been claimed by the presence of a third spin polarized band (absent in Bi(111)) and correspondingly five crossings with the Fermi level [3, 7–9], theoretically the number of crossings is also odd, but the configurations of the topological surface states do not include a third surface band [10, 11]. This additional band has been ascribed to result from imperfect surfaces [11].

Here, we experimentally examine the above debate using ARPES on Bi$_{1-x}$Sb$_x$ films. We optimized the in situ film growth method to minimize surface imperfections. We were able to control Sb concentration from $x = 0$ to $x = 0.6$ as Sb content is a critical parameter to determine the electronic properties of the Bi$_{1-x}$Sb$_x$ alloy. In order to have an overall view on the surface band structure, we tracked the evolution of the surface states not only near the $\overline{M}$-point but also around the $\overline{\Gamma}$-point. The ARPES results show on one hand a gradual evolution of the surface band structure from Bi(111) towards Sb(111), attesting precise control of the Sb content. On the other hand, we show that the third surface band could not be detected in the topological regime. Still, the corresponding surface band structure remains topological in accordance with the theory.

For the preparation of Bi$_{1-x}$Sb$_x$ samples, we have adopted an optimized growth procedure that produces high quality surfaces yielding sharp experimental band structure for Sb concentrations $0 \leq x \leq 0.6$. First, a 30 nm thick pure Bi(111) film is grown on a Si(111)-7×7 substrate. The sample is post-annealed at 500 K. As shown in Fig. [1]a, this growth method gives rise to a sharp and intense ARPES structure even at room temperature. On this buffer layer, we grow 120 nm thick Bi$_{1-x}$Sb$_x$(111) films. Bi and Sb are simultaneously deposited from Knudsen (effusion) cells. The Sb concentration has been determined from x-ray photoemission (XPS) spectra. An atomic sensitivity factor ratio ($K = 1.23$) has been used to find the Sb to Bi concentration ratio. The ratio $K$ was determined independently by energy dispersive x-ray spectroscopy (EDX). The ARPES measurements were performed with a hemispherical SPECS HSA3500 electron analyzer characterized by an energy resolution of about 10 meV. Monochromatized He I (21.2 eV) radiation was used as a photon source. The sample was measured either at 100 K or at room temperature to follow the dispersion of the surface states above the Fermi level.

Figure [1]c presents the experimental surface band-structure of Bi$_{1-x}$Sb$_x$ along the $l_1$ line (Fig. [1]b) as Sb concentration increases progressively from $x = 0$ to $x = 0.6$. In all the panels, the surface states $S1$ and $S2$ appear sharp and intense. The broad features below the surface states around the $\overline{\Gamma}$-point are surface resonances appearing within the projected bulk valence band [4–6, 12]. Figure [1]c nicely shows a gradual evolution of the surface band structure near the $\overline{\Gamma}$-point going from a pure Bi(111)-like to a pure Sb(111)-like band structure. As is known from the Bi(111) surface band structure, $S1$ and $S2$ lose spectral weight near the $\overline{\Gamma}$-point since they disperse into the projected bulk valence band [4–6, 12]. The crossing of the spin-split bands $S1$ and $S2$ can, therefore, not be discerned. The red dashed lines crossing at the $\overline{\Gamma}$-point in Fig. [1]c are an extrapolation of the experimental dispersion of $S1$ and $S2$ based on a theoretically calculated band structure of Bi(111) [13].

The surface band structure of Bi(111) in Fig. [1]c remains almost unchanged when increasing $x$ from 0 to 0.16. For $x > 0.22$, a deformation of the $S1$ dispersion occurs: The effective mass $m^*$ of $S1$ changes sign at $x = 0.28$. In order to analyze the evolution of $m^*$ of $S1$ as a function of Sb concentration, we fitted its dispersion with a symmetric power func-
FIG. 1: (a) Surface state band structure of Bi(111) along the ΓM direction (line l2, Fig. 1b) and the corresponding Fermi surface recorded at 300 K. (b) Higher panel, schematic representation of the 3D and 2D Brillouin zones of Bi crystal and its (111) surface. Lower panel, schematic representation of the Fermi surface of Bi(111). The dashed lines denoted by l1, l2, and l3 represent the different momentum directions along which the band structures have been recorded. l3 corresponds to \( k_x = 0.667 \, \text{Å}^{-1} \), i.e., at a polar angle of 18° using a He I light source. (c) and (d) Evolution of the experimental surface band structure of Bi\(_{1-x}\)Sb\(_x\)(111) as a function of \( x \) near Γ along ΓK (line l1, Fig. 1b) and near M along line l3 in 1-c, respectively. The red dashed lines on the surface states are guides to the eye. The Sb concentration \( x \) is indicated for measurements performed at 100 K in black and at 300 K in red.

The evolution of the experimental band structure of the surface states along the l3 line near the M-point is shown in Fig. 1d as a function of Sb content. The bands are sharp and intense, but seem to not deviate much from the pure Bi(111) band dispersion in the entire concentration range, except at \( x = 0.6 \), where they become faint and washed-out. This broadening and intensity loss is not related to the surface quality of the sample, since the bands are very sharp around Γ (Fig. 1c). We have analyzed the energy distribution curves (EDC) at \( k_y = 0 \) of the band structures in Fig. 1d by fitting a Voigt function to the spectral features of the S1 and S2 bands (Fig. 2d). The energy positions of S1 and S2 (Fig. 2e) evolve smoothly as \( x \) increases. The binding energy of S1 varies from \( E_B \approx 30 \, \text{meV} \) for pure Bi, goes to a minimum of \( E_B \approx 15 \, \text{meV} \) for \( x \approx 0.2 \), then increases again and reaches \( E_B \approx 40 \, \text{meV} \) at \( x \approx 0.6 \). Similarly, the S2 energy position decreases slowly from \( E_B \approx 140 \, \text{meV} \) at \( x = 0 \) to a minimum \( E_B \approx 90 \, \text{meV} \) for an Sb content of \( x \approx 0.4 \) and then increases again to \( E_B \approx 120 \, \text{meV} \) at \( x \approx 0.6 \). We note that the TI region does not constitute any special stage in the evolution of S1 and S2 energy positions [3, 8, 16, 17]. In order to check for any hidden phenomena within the linewidth of the two surface bands, we analyzed the linewidth (full width at half maximum...
dential broadening within the TI region. This observation is different from previous ARPES results that indicate an additional S1 broadening \[ \delta \] 9 18 19. Those ARPES measurements show the presence of a weak contribution to the linewidth of S1 for \( x \approx 0.13, 0.16, 0.17 \), and 0.21 \[ \delta \] 9 18 19. An extra broadening of S1 could agree with the appearance of a third spin-polarized surface band (S3), which would result in five crossings with the Fermi level proving the non-trivial topology classification of the system as indicated in Ref. 3 7. However, the expected energy position of S3 is about 45 meV from S1 at \( k_x = 0.67 \ \hat{A}^{-1} \) \[ \delta \] 3 7. With a linewidth of S1 of about 40 meV, a shoulder near the S1 peak in the EDC curves corresponding to S3 should be observable. Here, neither a peak nor a shoulder corresponding to S3 could be resolved. In addition, no indication of the presence of S3 even above the Fermi level can be seen in any of the ARPES data recorded at room temperature (see Fig. 2 e and f, Fig. 2 f). On the other hand, comparing the APRES results where S3 has been detected, a certain inconsistency about S3 can be observed: A) S3 has different dispersions along the \( \Gamma M \) direction in the literature \[ \delta \] 3 7 9 18 19. B) The reported energy separation between S1 and S3 at \( k_x \approx 0.67 \ \hat{A}^{-1} \) has different values ranging from 11 meV to 45 meV \[ \delta \] 3 7 9 18 19. Hence, in contrast to S1 and S2, the detection of S3 seems to be not easily reproducible and to be more sporadic than systematic. Yet, the presence of S3 is not the ultimate proof of the non-trivial topology of the insulating BiSb alloy. Ab initio and tight-binding calculations describe the topological phase with only S1 and S2 \[ \delta \] 10 11. Furthermore, the observed S3 in the experiment has not been related to the non-trivial topology but to surface imperfections \[ \delta \] 9 11. S3 can originate, for example, from locally different surface terminations \[ \delta \]. Thus, the uncontrolled damage to the surface caused by crystal cleaving can explain the sporadic character of S3. In this regard, the results presented here from in situ grown films with comparatively reduced surface damage are closer to the realistic representation of the topological insulator Bi\(_{1-x}\)Sb\(_x\).

With the absence of S3 in the non-trivial topological phase, S1 cannot hybridize with S3, but merges into the conduction band near the \( \overline{M} \)-point. The number of crossings with the Fermi level is still odd (five) \[ \delta \] 9 11. It ensues that the electron pocket at \( \overline{M} \) does not enclose the \( \overline{M} \)-point in the Fermi surface \[ \delta \] 3 7 11. In Fig. 3, the measured Fermi surfaces of Bi\(_{0.91}\)Sb\(_{0.09}\) and Bi\(_{0.99}\)Sb\(_{0.01}\), which belong to the TI region are plotted. Closing electron-pockets contours just before the \( \overline{M} \)-point can be discerned, especially for \( x = 0.09 \). For \( x = 0.11 \), the size of the electron pocket is smaller (Fig. 2 c) preventing us from resolving its contour outline. On the corresponding experimental surface band structures along \( \overline{\Gamma M} \) shown in the lower panels, the intensity of S1 and S2 vanishes at \( \overline{M} \) (Fig. 3). The red dashed lines are a guide to the eye. In addition, also the experimental band structure for Bi\(_{0.1}\)Sb\(_{0.9}\) in Fig. 3 clearly shows a closed contour of the electron pocket and S1 merging into the conduction band before \( \overline{M} \). Consequently, the experimental surface band structure of the topo-

**FIG. 2**: Evolution of different parameters as a function of Sb concentration. (a) Surface state band structure along the \( l \) line (Fig. 1 b) of Bi\(_{0.88}\)Sb\(_{0.12}\) and Bi\(_{0.44}\)Sb\(_{0.56}\) with the corresponding fitting curves (orange) to the dispersion of S1. (b) Inverse effective mass \( 1/m^* \) at \( k_F \) obtained from the fit of S1 dispersion around \( \Gamma \). Estimated binding energy \( E_B \) of the S1 and S2 crossing at the T-point. (c) Fermi vector \( k_F \) along \( k_x \) (square symbols) and \( k_y \) (round symbols) of the electron pocket around the \( \Gamma \)-point and of the second electron pocket near \( \overline{M} \) along the \( l_3 \) line (blue triangular symbols). The sketch on the upper side of the graph representing a Fermi surface of Bi(111) along \( \overline{\Gamma M} \) is a graphical legend of the graph. (d) Example of the fit of EDCs at \( k_y = 0 \ \hat{A}^{-1} \) along the \( l_3 \) line from Bi\(_{0.91}\)Sb\(_{0.09}\) measured at 300 K. The fit curves are S1 and S2 (red) and background contributions (dashed-gray). (e) Energy peak positions of S1 and S2 in the EDCs at \( k_y = 0 \ \hat{A}^{-1} \) of the band structure recorded along the \( l_3 \) line. (f) Corresponding extracted line widths of S1 and S2 peaks. The yellow zone indicates the TI region. The filled symbols in (e) and (f) indicate room temperature data points.

(FWHM) for each spectral feature. The extracted evolution of the linewidth for S1 and S2 is also smooth as shown in Fig. 2 f. The band S1 is characterized by a smaller linewidth than S2, which is most probably due to a longer quasiparticle lifetime near the Fermi level. For \( x = 0 \), S1 has a linewidth of about 40 meV, which stays almost constant with increasing Sb content until \( x = 0.4 \). For \( x > 0.4 \), it increases comparatively rapidly to around 80 meV at \( x = 0.6 \). The linewidth of S2 follows the behavior of S1 with constant values around 55 meV until \( x \approx 0.4 \), after which it increases to about 140 meV at \( x = 0.6 \).

We note that the linewidth of S1 does not show any add-

Waxman et al. [20] stated that for example, from locally different surface terminations [20]. Thus, the uncontrolled damage to the surface caused by crystal cleaving can explain the sporadic character of S3. In this regard, the results presented here from in situ grown films with comparatively reduced surface damage are closer to the realistic representation of the topological insulator Bi\(_{1-x}\)Sb\(_x\).
FIG. 3: Fermi surface (upper panels) and corresponding experimental surface band structure along the $\Gamma M$ direction (lower panels) of Bi$_{0.91}$Sb$_{0.09}$ (300 K), Bi$_{0.80}$Sb$_{0.11}$ (100 K), and Bi$_{0.70}$Sb$_{0.30}$ (100 K). The insets are to indicate the closing electron-pocket contour before the $M$-point.

FIG. 4: Schematic representation of the main phases during the evolution of the band structure of Bi$_{1-x}$Sb$_x$(111) surface with increasing Sb concentration. The upper panels are the corresponding Fermi surface representations.

logically non-trivial phase of Bi$_{1-x}$Sb$_x$(111) is in agreement with the theoretical modeling presented in Ref. 11.

We conclude that the defect-reduced Bi$_{1-x}$Sb$_x$(111) surface bears only two surface states $S1$ and $S2$ regardless of Sb concentration $x$. We schematically present the evolution of the surface states $S1$ and $S2$ as a function of Sb content $x$ in Fig. 4. For pure Bi(111) (Fig. 4-a), $S1$ has been considered to connect to the valence band at $M$ [21]. It switches connection from the valence band to the conduction band near $M$ at the topological transition ($x = 0.04$) (Fig. 4-b). The surface state bands $S1$ and $S2$ further adapt to the energy shift of the bulk bands as Sb content increases. They smoothly evolve from a Bi(111)-like dispersion to the characteristic Sb(111)-like band structure (Fig. 4-c). This adaptation is most visible around $\Gamma$ within $0.13 \lesssim x \lesssim 0.28$. However, it is not until $x \approx 0.6$ that $S1$ and $S2$ become broad and faint near $M$ indicating convergence to the Sb(111) band structure (Fig. 4-d) [7, 23].

In summary, following an optimized method to grow high quality Bi$_{1-x}$Sb$_x$(111) films, we have investigated the evolution of the surface states of the system by a variation of $x$ from 0 to 0.6 using ARPES. Around $\Gamma$ the ARPES data show a gradual evolution of the surface band structure from Bi(111) towards Sb(111). The previously reported third surface band near $M$ could not be detected in the topologically insulating phase here. We find our results of the experimental Bi$_{1-x}$Sb$_x$(111) surface state band structure to agree with available theoretical predictions, which identify the crystal as topologically non-trivial with two surface states.

We acknowledge stimulating discussions with A. Schnyder. H. M. B. acknowledges funding from the Deutsche Forschungsgemeinschaft (DFG). C. R. A. acknowledges funding from the Emmy-Noether-Program of the Deutsche Forschungsgemeinschaft (DFG).

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