SUPPLEMENTAL MATERIAL FOR

Spectroscopic signature of surface states and bunching of bulk sub-bands in topological insulator \((\text{Bi}_{0.4}\text{Sb}_{0.6})_2\text{Te}_3\) thin films

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I. SUBSTRATE TREATMENT

Firstly the \(\text{SrTiO}_3\) (111) substrates are polished by means of a lens tissue and isopropanol to ensure a clean surface. Following this cleaning step, the \(\text{SrTiO}_3\) substrates undergo a buffered hydrofluoric acid (BHF) treatment to ensure \(\text{Ti}^{4+}\) terminated surface. The \(\text{SrO}^4^-\)\(\text{S}_3\) surface termination is etched by an ultrasonic immersion of the substrates in demineralized water for 30 min, allowing the formation of \(\text{SrH}\) compounds. These compounds are subsequently selectively etched by a 30 s BHF dip. Next, the substrates are polished again by a lens tissue and isopropanol. To obtain a terraced surface, the chemical treatment is succeeded by a heat treatment in a tube furnace, where the substrates are heated to 950 °C for 1.5 h, while maintaining an oxygen rich environment by applying an oxygen flow of 150 ml/min [1]. The treated substrates from this study typically exhibit terraces with a width of approximately 100 nm.

To avoid charging effects during ARPES measurements, as well as to enable a tunneling current to be established on our \((\text{Bi}_{0.4}\text{Sb}_{0.6})_2\text{Te}_3\) films deposited on insulating \(\text{SrTiO}_3\), a 5 nm W film is sputter deposited on the edge of the substrate by means of a hard mask. These strips are connected to the sample holder, which allows for an electronic connection between the film and the holder. The final substrate treatment step, prior to the film deposition, is an in-situ anneal performed for 1 h at 550 °C in a Te rich environment.

II. ARPES SELECTION RULES TO EXPLAIN ASYMMETRY IN EDM

The ARPES intensity can be linked to the electronic structure that is obtained within our virtual crystal (VC) approximation, by

\[
I(\epsilon, \mathbf{k}) \propto \sum_{n\sigma} \delta (\epsilon - \epsilon_{nk}) \left| \mathbf{A} \cdot \mathbf{P}_{nk}^\sigma \right|^2. 
\]

As no spin is detected in the experiment, we need to sum over the spin degrees \(\sigma\) of the spinors \(\psi^\sigma_{nk}\) that enter in the transition matrix elements describing the excitation probability from bound to propagating states. These are given by

\[
\mathbf{P}_{nk}^\sigma = \langle e^{i\mathbf{k} \cdot \mathbf{r} - \kappa z} | -i\hbar \nabla | \psi^\sigma_{nk} \rangle. 
\]

This expression reflects the dependence on the polarisation \(\mathbf{A}\) of the exciting photons. It also accounts for the conservation of parallel crystal momentum \(\mathbf{k}\), while the energy conservation and the energy dependent escape depth of the emitted electron is effectively included through \(\kappa(\epsilon, \mathbf{k})\). For \(p\)-polarized light at oblique angle of incidence \(\theta\), and \(\mathbf{k} \parallel \hat{z}\) (along \(\Gamma\)-K), the transition matrix elements of eq. (2) naturally decompose into in-plane \(x\)-, and out-of-plane \(z\)-components,

\[
\mathbf{A} \cdot \mathbf{P} \propto P_x \cos \theta + P_z \sin \theta. 
\]

States that have identical parity for \(P_x\) and \(P_z\) upon inversion of \(\mathbf{k}\) or have exactly one of these elements zero due to symmetry, will show up as symmetric features in the ARPES image, whereas only states with both elements nonvanishing and of opposite parity may show up as asymmetric features, provided symmetry is not restored in the...
ARPES by multiple degenerate contributions in the summation of eq. (1). We will now show that (i) the Bi/Sb topological surface state, which shows up as symmetric, is of the former class, (ii) the Te surface state, which shows up as asymmetric, is of the latter class, and (iii) that the bunched bulk-like states feature is symmetrized by degeneracy.

In our VC calculations, we find that the momentum matrix components,

$$\mathbf{P} = (P^\uparrow_x, P^\downarrow_x) \hat{x} + (P^\uparrow_y, P^\downarrow_y) \hat{y} + (P^\uparrow_z, P^\downarrow_z) \hat{z},$$

(4)

transform under inversion of the \( k \) labels, into

$$\bar{\mathbf{P}} = e^{i\phi} \left( (-P^\uparrow_x^*, P^\downarrow_x^*) \hat{x} + (P^\uparrow_y^*, -P^\downarrow_y^*) \hat{y} + (-P^\uparrow_z^*, P^\downarrow_z^*) \hat{z} \right).$$

(5)

It turns out that the contribution of the Bi/Sb topological surface state to the ARPES intensity is well described by a single \( \mathbf{P} \)-vector,

$$I(\epsilon_{tss}, \mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{P}|^2.$$

(6)

For small \( \mathbf{k} \), we get that \( P^\uparrow_y \approx -i P^\uparrow_x \in \text{Re}, \ P^\downarrow_y \approx i P^\downarrow_x \in \text{Re}, \) and \( P^\uparrow_z, P^\downarrow_z \approx 0 \), where the relations become exact for \( \mathbf{k} = 0 \). As a result, this \( \mathbf{P} \) is circularly polarized and oriented in-plane, and thus \( |\mathbf{A} \cdot \mathbf{P}|^2 \approx |\mathbf{A} \cdot \bar{\mathbf{P}}|^2 \) near \( \Gamma \). This immediately results in a symmetric appearance of the topological surface state that is visible near \( \Gamma \) in the ARPES.

A similar analysis shows that the same holds for the Te surface state. However, this state is visible at much larger \( \mathbf{k} \)-vectors, where an asymmetric component in the \( p \)-polarized ARPES develops due to nonvanishing \( P^\downarrow_z \)-components away from \( \Gamma \), in combination with a notable difference in magnitude for the various spin-up and spin-down components. The \( |\mathbf{A} \cdot \mathbf{P}|^2 \) at \( \mathbf{k} \) and \( |\mathbf{A} \cdot \bar{\mathbf{P}}|^2 \) at \(-\mathbf{k}\) become very different at larger \( \mathbf{k} \) due to this out-of-place component, which is not balanced by spin symmetrization. This explains the observed asymmetry.

Finally we consider the observed symmetric intensity of the nearly degenerate (bunched) bulk-like bands. Their combined contribution to the ARPES intensity near \( K/8 \) is found to be well described only by a combination of two vectors, being \( \mathbf{P} \) and the symmetry related \( \bar{\mathbf{P}} \),

$$I(\epsilon_{bbb}, \mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{P}|^2 + |\mathbf{A} \cdot \bar{\mathbf{P}}|^2.$$

(7)

Upon inversion of the \( \mathbf{k} \)-label, the role of \( \mathbf{P} \) and \( \bar{\mathbf{P}} \) is merely interchanged, resulting in an unaltered intensity. This feature therefore has a \( p \)-polarized ARPES intensity that is expected to be symmetric under inversion of \( \mathbf{k} \). Finally we remark that in all three cases, we find the magnitudes of the \( P \)-vectors to be comparable. The observed intensity difference is therefore not explained by this analysis, and should be attributed to other effects.
FIG. 1. Calculated band structures for free-standing thin slabs of 5 to 10 QL (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$. The calculations show that the energy position of the Dirac point in the topological surface states (green lines), as well as the position at which the bulk states bunch (blue lines) and the Te surface state dispersion (red lines) are independent of thickness. This observation allows us to unambiguously compare the ARPES data with the STS data acquired on 10 and 5 nm films respectively.
IV. LASER-ARPES

FIG. 2. ARPES spectra of 10 nm (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ thin film deposited on SrTiO$_3$, using a photon energy of $h\nu = 6.2$ eV. The EDMs show the clear Dirac cone surface state dispersion in the parallel reciprocal space dimensions, $k_x$ (a) and $k_y$ (b). The FS maps present the constant energy contours at binding energies indicated by the dotted lines in the left EDM (i)-(iv). To enhance the signal to noise ratio, the EDM show the combined signal of a range of 0.03 (1/Å) in the perpendicular $k_\parallel$ direction, and the FS maps a range of 30 meV around $E - E_F = 0.0$, -0.05, -0.1, and -0.15 eV.

V. DIRAC VELOCITY DETERMINATION BY SCANNING TUNNELING SPECTROSCOPY

As shown in ref. [2] scanning tunneling spectroscopy can also provide information on the dispersion of the energy bands in momentum space. By measuring inverse decay length $\kappa(V)$, $k_\parallel$ can be extracted using equations (3) and (4) from the manuscript. Using the relation $E - E_D = e(V - V_D) = \hbar v_F |k|$ = $\hbar v_F k_\parallel$, where $E_D$ refers to the location of the Dirac point, the Fermi velocity, $v_F$, in the vicinity of the Dirac point can be determined. We find a $v_F$ of about 1.5 ± 0.5 x 10$^5$ m/s, which is substantially smaller than the $v_F$ extracted from the ARPES spectrum. Bearing in mind that the TB calculations reveal a non-linear dispersion of the topological surface states in the vicinity of the Dirac point one expects a decrease in $v_F$ upon decreasing the energy window near the Dirac point. Therefore, we would like to emphasize that both $v_F$ as extracted from the STS as well as from the ARPES experiments agree very well with the TB calculations.

VI. ADDITIONAL SCANNING TUNNELING SPECTROSCOPY MEASUREMENT

Fig. 3 shows an STS measurement recorded on another 5 nm thin (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ film than the one presented in Fig. 4 in the main text. This measurement also shows an oscillatory behavior of the dI(V)/dV signal. We can distinguish three clear peaks in the DOS at -0.26 V, -0.40 V and -0.57 V. Although the peak energies are shifted by about 0.04 V with respect to the measurement of Fig. 4(c), they can still be explained by the TB slab calculation and STS simulation of Fig. 4(a) and (b) respectively. Likewise, the first peak originates from the bunching of states just below the DP, the second peak from the Van Hove singularity of the upper red surface state and the broad third peak from the combined surface states at lower energies. The aforementioned shift of the energies is most likely due to a tiny amount of adsorbates or Te vacancies, which both lead to doping of the thin film. The inset in Fig. 3 shows a zoom of the dI(V)/dV curve around the linear slope observed above the top of the VB. The DOS at -0.13 V is highly reduced with respect to the rest of the bias voltage range. The correlation of the TB calculations with this STS measurement reveals that this linear behavior of dI(V)/dV likely originated from the linearly dispersive surface states. The steep slope at bias voltages below the DOS minimum can be ascribed to the presence of the bunched states near the top of the VB.
FIG. 3. STS $dI(V)/dV$ and $(dI(V)/dV)/(I/V)$ measurements recorded on a 5 nm thin $(\text{Bi}_{0.4}\text{Sb}_{0.6})_2\text{Te}_3$ film (different sample than the measurement from Fig. 4). The normalized curve shows peaks at -0.26 V, -0.40 V and -0.57 V. The inset shows a zoom of the $dI(V)/dV$ curve, visualized by the dotted box, which shows a minimum in the DOS. The increase in DOS is larger below this minimum than above it due to the presence of the bunched states originating from the $(\text{Bi}_{0.4}\text{Sb}_{0.6})_2\text{Te}_3$ film.

REFERENCES

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