Spectroscopic signature of surface states and bunching of bulk subbands in topological insulator (Bi$_{0.4}$ Sb$_{0.6}$)$_2$ Te$_3$ thin films


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I. INTRODUCTION

Chalcogenide three-dimensional (3D) topological insulators (TIs), such as Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃, are well-known for their topological surface states (TSSs) [1–3]. These metallic surface states, which are characterized by a linear dispersion as well as spin-momentum locking, appear as a Dirac cone at the Γ point. Since Bi₂Te₃ single crystals are intrinsically n-doped, and Sb₂Te₃ p-doped, alloys of the two have been developed to engineer a material in which the chemical potential is located within, or close to, the bulk band gap [4]. An advantage of a higher Sb/Bi ratio is the shift of the Dirac point (DP) to higher energies, reaching above the Fermi energy (EF) [5].

Due to the spatial extent of the surface state in the z direction, it has been predicted that ultrathin slabs of 3D TIs provide a route to a hybridization gap around the DP [6,7], thereby gaps out the TSSs and paving the way to topologically protected one-dimensional (1D) edge-state transport, very comparable to the quantum spin Hall (QSH) effect in HgTe quantum wells [8–10]. Even though Bi₂Se₃ presents the largest bulk band gap, Bi₂Te₃ and Sb₂Te₃ are predicted to be more appealing candidates to exhibit 1D transport due to their relatively short edge-state decay length in the ultrathin film limit [7,11,12]. While stoichiometric slabs have been well-investigated spectroscopically [13–15], even in the limit of hybridized surface states [16], the electronic structure of ultrathin films of off-stoichiometric (Bi₁₋ₓSbx)₂Te₃ is still relatively unexplored. Zhang et al. [5] studied the influence of the stoichiometry on the electronic properties of ultrathin (Bi₁₋ₓSbx)₂Te₃ by means of angle-resolved photoemission spectroscopy (ARPES) and transport measurements. They show that band structure can be engineered by changing the stoichiometry. Furthermore, quasiparticle interference patterns have been imaged with a scanning tunneling microscope, revealing the dispersion above the Fermi energy (EF) [17,18].

Here, we investigate the electronic structure of few-nm (Bi₁₋ₓSbx)₂Te₃ by directly comparing the results of multiple techniques. We performed ARPES measurements, scanning tunneling spectroscopy (STS) measurements and ab initio tight-binding (TB) calculations. The good agreement between the measured and calculated electronic structure reveals a bunching effect of the bulk sublevels, the identification of Bi/Sb TSSs, as well as Te surface states close to the top of the VB, leading to strong peaks in the density of states (DOS). The modeling shows that for (Bi₁₋ₓSbx)₂Te₃ with x = 0.6, the reduced bandwidth is likely caused by a Sb/Bi substitution-induced inversion of the band order near the high-symmetry point Γ. This inversion interchanges the bands close to EF, while the order at the Z point remains unaltered.

II. MATERIALS AND METHODS

A. Molecular beam epitaxy

For this study, 5 and 10 nm (Bi₁₋ₓSbx)₂Te₃ films were deposited using molecular beam epitaxy (MBE) on gate-tunable, Ti-terminated SrTiO₃ (111) substrates in a deposition chamber with a base pressure of about 5.0 × 10⁻¹¹ mbar. Details on the substrate treatment [19] can be found in the Supplemental Material (SM) [20]. High-purity Bi (6N), Sb (6N), and Te (6N) were evaporated from standard Knudsen effusion cells. During the deposition, the substrate was held at a temperature of 225 °C. A quartz crystal microbalance was used to calibrate the individual material fluxes. To ensure a high crystalline growth while suppressing the amount of Te vacancies, we employed a flux ratio of (Bi+Sb):Te = 1:10, with a
deposition rate of 0.07 nm/min. To verify the stoichiometry of the deposited film, in situ x-ray photoelectron spectroscopy (XPS) spectra were recorded using an Omicron nanotechnology surface analysis system, equipped with a monochromatic aluminium source (Kα x-ray source XM1000).

B. Angle-resolved photoemission spectroscopy
ARPES data were acquired at the Van der Waals-Zeeman Institute. The ARPES spectra are taken at a base temperature of 15 K, using an L1 He-Lamp, emitting linearly, p-polarized photons with an energy of 21.2 eV, and an A-1 hemispherical analyzer, both from MB Scientific. The system is equipped with a TMM 304 UV monochromator from Specs. The energy resolution was 15 meV and the angular resolution better than 0.1°. Laser-ARPES spectra were obtained using a fourth harmonic source from APE GmbH, producing 200 nm photons with a corresponding energy of 6.2 eV, with an energy resolution of 5 meV and a k-resolution of 0.002 Å⁻¹. The measurements were performed while maintaining a pressure of <5.0 × 10⁻¹¹ mbar.

C. Scanning tunneling spectroscopy
Scanning tunneling microscopy (STM) and spectroscopy measurements were performed at 77 K with a low-temperature Omicron ultrahigh vacuum (UHV) STM. The base pressure of the STM chamber was below 1.0 × 10⁻¹¹ mbar and PtIr tips were used. The I(V) spectroscopy experiments were conducted in the constant height mode, i.e., the tunnel current was measured while the sample bias was ramped with the feedback loop disabled. The (normalized) dI(V)/dV curves are the numerical derivatives of the I(V) recordings. The dI(V)/dV and (dI(V)/dV)/(I(V)/V) curves were obtained by averaging over many I(V) traces recorded at different locations.

D. Ab initio tight-binding modeling
The electronic structure of the ternary tetradyminate alloy was obtained using a TB approach based on the ab initio Green’s function calculations of Aguilara et al. [21]. Their projected TB parameters turn out to be very similar for pristine Bi₂Te₃ and Sb₂Te₃ [22], resulting in very comparable band dispersions, apart from band inversions along the line Γ – Z. This close resemblance allows us to interpolate to the alloy system in the following way: the quasiparticle states for the alloy are expanded as wave packets of Bloch-like sums of localized functions:

$$\psi(r) = \sum_{mk} \epsilon_{mk} \phi_{mk}(r),$$

$$\phi_{mk}(r) = \frac{1}{\sqrt{N}} \sum_{R} e^{i k \cdot R} w_{m}(r - R).$$

The w_m(r) centered on a Bi or Sb atom are derived, respectively, from the projected Wannier functions of the pristine Bi₂Te₃ or Sb₂Te₃ crystals, and when on a Te atom, from either one. The alloy disorder is thus incorporated into this mixed basis, which can reasonably be assumed to inherit the orthogonality of the pristine Wannier functions. The alloy Hamiltonian elements on the k diagonal then reduce to the weighted average of the pristine ones. As these are by far the largest terms, they effectively define a virtual crystal (VC) Hamiltonian for the alloy. The alloy disorder further enters via smaller off-k-diagonal elements that may be accounted for in a perturbative expansion. These off-diagonal terms will cause the wave packets to spread over a range of k vectors centered around the VC one. As it turns out, it suffices to compute the VC band structure, {εmk, ψmk}, to identify the main features in the ARPES measurements. Similarly, we compute the laterally averaged local density of states (LDOS) and use the Tersoff-Hamann model [23] to simulate the marginal tunnel currents:

$$\frac{dI}{dV} \propto \sum_{nk} \delta(\epsilon_{nk} - eV)e^{-2k\cdot z}|\psi_{nk}|^2.$$

Here the quasiparticle amplitudes at the outermost Te atoms are used to generate the LDOS at the tip position z (9 Å), while accounting for the k- and εnk-dependent inverse decay length κnk, satisfying

$$\kappa_{nk} = \sqrt{\frac{2m}{\hbar^2} \left( \Phi - \frac{1}{2} \epsilon_{nk} \right) + k_z^2},$$

in which Φ (5.4 eV) is the work function. This simulated signal can be decomposed into layer contributions, as in Fig. 4(b), by adding a projective weight vₖₙₜ = |⟨\psi_{nk} | A⟩|^2 to the summand for atomic layer A. The same projective weight is used to identify and color code the surface states in the band dispersion in Figs. 2, 3(b), 4(a), and S1.

E. Vacuum transfer
To avoid surface contamination and oxidation, we have transferred the thin films from the MBE system to the XPS, STM, and ARPES systems using a UHV suitcase. The vacuum suitcase is equipped with a nonevaporable getter pump and an ion pump, which together ensured the pressure remained below 1.5 × 10⁻¹⁰ mbar during the transfer process. In the ARPES system, the film has briefly been exposed to a pressure of 3.0 × 10⁻¹⁰ mbar during the transfer of the sample from the suitcase to the main chamber. For a film to arrive at the STM main chamber, the sample has to move through a load lock and preparation chamber with a base pressure of 5.0 × 10⁻⁹ mbar and 1.0 × 10⁻¹⁰ mbar, respectively.

III. RESULTS AND DISCUSSION

(Bi₁₋ₓSbx)₂Te₃ crystallizes in the rhombohedral tetradyminate crystal structure, as depicted in Fig. 1(a). The (Bi₁₋ₓSbx)₂Te₃ surface-matched unit cell is composed of three quintuple layers (QLs), each of which are approximately 1 nm high and separated from each other by a Van der Waals gap. The QLS consist of five atomic layers in a Te-X-Te-X-Te stacking, where X can either be Bi or Sb. The STM constant current image in Fig. 1(b) reveals the film’s surface morphology. The film exhibits triangular islands, reflecting the threefold symmetry of the crystal structure, with single QL terrace step edges, visible in the line profile shown in Fig. 1(c). The 0.2 nm height differences observed in the
FIG. 1. (a) The layered rhombohedral tetradymite crystal structure of \((\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3\) revealing the quintuple layer stacking along the \(c\) axis, which are weakly bonded via Van der Waals interaction. (b) STM topography image (250 x 250 nm) of a 5 nm \((\text{Bi}_{0.4}\text{Sb}_{0.6})_2\text{Te}_3\) film measured at a bias voltage of 1.0 V and a current set point of 400 pA. The inset shows a STM topography image (15 x 15 nm) with the atomic structure on a single terrace measured at a bias voltage of 0.2 V and a current set point of 1.0 nA. The hexagonal structure as shown in (a) is clearly visible. (c) Line profile taken at the white line of the main figure of (b) which crosses a stack of triangular terraces. The height difference at every step edge is approximately 1 nm. The middle terrace is slightly tilted. (d) Line profile taken at the white line of the inset of (b).

A. Ab initio tight-binding modeling

The electronic structure of the \((\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3\) alloys was obtained within the VC approximation of the \textit{ab initio} TB model as outlined above. All slab calculations were performed on free-standing vacuum-surrounded slabs. For the modeling, we take into account all six \(p\)-type spin orbitals of every atom in the unit cell, which contains only a single QL for the 3D bulk systems. The covalent bonding inside the QL gives rise to 15 doubly degenerate VBs, of which nine are occupied and six unoccupied, separated by a small gap along the line \(F - Z\). We refer to Zhang et al. for a schematic of both the bulk and surface Brillouin zones, showing labels for the high-symmetry points [27]. The dispersion along line \(\Gamma - Z\), i.e., in the direction perpendicular to the QLs, is small due to the van der Waals bonding in between the QLs. In the pristine \(
\text{Bi}_2\text{Te}_3\) bulk crystal, we find that the top VB has an energy at \(\Gamma\) that is well below its energy at the \(Z\) point. In pristine \(\text{Sb}_2\text{Te}_3\), the reverse order is obtained. Upon sufficient alloying, we find that in our VC calculations the band order along \(\Gamma - Z\) can be tuned, causing the band dispersion along this line to nearly vanish at intermediate alloy fractions close to 0.6.

FIG. 2. \textit{Ab initio} TB calculations for a six-QL free-standing thin slab of \((\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3\) in the \(M - \Gamma - K\) direction for (a) \(x = 0.0\), (b) \(x = 0.6\) and (c) \(x = 1.0\). The energy is plotted with respect to the predicted \(E_F\). The green, red, and blue lines, respectively, represent Bi/Sb surface states, Te surface states, and states with a bulk character. The grey area marks the projected bulk bands. All states outside this projection represent surface states. The calculations visualize the characteristic shift of the DP with respect to the top of the VB. Furthermore, they show that for mixed stoichiometries, especially close to \(x = 0.6\), the bulk states bunch at an energy close to \(-0.2\) eV.
FIG. 3. Correlation between TB calculations and ARPES measurements. (a) ARPES EDM of the band dispersion along the $\bar{K} - \Gamma - \bar{K}$ direction of a 10 nm (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ film deposited on a SrTiO$_3$ (111) substrate. The V-shaped dispersion, at energies above $-200$ meV, originates from the TSS. The relatively weak M-shaped dispersion just below it, at $-200$ meV $< E - E_F < -400$ meV, is from the bulk VB. At energies below $-500$ meV, the Te surface state shows up, which is flanked by bulklike intensity at lower energies. The DP is located in the vicinity of the top of the bulk VB. (b) Ab initio TB calculations for a free-standing thin slab, ten QL of (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$, in the $K - \Gamma - K$ direction. The $y$ axis presents the energy of the electronic states with respect to the predicted $E_F$, resulting from the TB calculations. To allow for a proper comparison between the experimentally observed and theoretically predicted band structure, the TB slab calculation is plotted up until a crystal momentum of K/4 which corresponds to the measured range of 0.25 Å$^{-1}$ in the ARPES EDM.

Fig. 2, with a striking reduction of the bandwidth around the $\Gamma$ point visible in Fig. 2(b).

In addition, TSSs develop from the bulk bands, which separate from these bulklike bands into the gaps that open near $\Gamma$. These surface states are only weakly sensitive to the number of QLs. As these surface states live on either side of the slab and decay exponentially into the bulk, the development of...
the bonding-antibonding gap at $\Gamma$ is indicative for the decay length. We estimate the decay length to be about three QLs, with an odd-even difference due to the nodal plane inside or in between the middle QLs.

The electronic structure of the slabs, as depicted in Figs. 2, 3(b), 4(a), and S1 are indeed mainly composed of closely spaced parallel bands inside each projected 3D-bulk band (grey) with predominantly bulk character (blue) and a fixed number of surface states that lie outside the projected bulk bands. These surface states are colored green if they have a large weight on the outermost Bi/Sb atoms and red if on the outermost Te layer. The Bi/Sb surface state develops a Dirac cone at $\Gamma$ for increasing slab thicknesses, as shown in Fig. S1, and is termed TSS. The reversal of the band order at $\Gamma$ causes the DP to shift from buried inside the VB for Bi$_2$Te$_3$ to slightly above the VB for Sb$_2$Te$_3$, see Fig. 2.

In the VC approximation, the top- VBs have small energy dispersions over a considerable portion of the Brillouin zone. Such nearly flat bands can easily be localized, and will thus be more sensitive to local disorder in the alloy. This disorder needs to be included in the perturbation expansion going beyond the VC approximation. Furthermore, the additional degeneracy caused by the bunching of these flat, bulklike bands brings about localization not just in the lateral direction but also in the perpendicular direction. This makes them even more susceptible to the alloy disorder. The vicinity of these bands to the DP may cause hybridization of these bands with the TSS, potentially interfering with the delocalized nature of the TSS.

**Angle-resolved photoemission spectroscopy**

To study the electronic band structure, ARPES measurements have been performed on a nominal 10 nm (Bi$_{0.5}$Sb$_{0.6}$)$_2$Te$_3$ film. The resulting electron distribution map (EDM) measured along the $\bar{K} - \Gamma - \bar{K}$ direction is presented in Fig. 3(a). On the same film, laser-ARPES measurements were conducted. These results confirm the linearly dispersing TSSs, along with a circular constant energy contour throughout the occupied part of Dirac cone, see Fig. S2. The conformity of the TB model calculations on a vacuum-surrounded slab to the ARPES data from a film of similar thickness, shown in Fig. 3, is striking. The small discrepancy between the $E_F$ in the ARPES EDM and the TB slab calculation can be explained by surface adsorption of residual gases, which is likely to take place when the sample is cooled down to 15 K, at which temperature the ARPES measurements were performed [28]. Additionally, the effect can also be attributed to defects present in the (Bi$_{0.5}$Sb$_{0.6}$)$_2$Te$_3$ film. A more in-depth description regarding the observed discrepancy in $E_F$ will follow in the next section. The TSS are relatively weak but clearly resolved in the ARPES EDM at energies above $-200$ meV, and merge on the lower binding energy side with weak bulklike states between $-200$ meV and $-400$ meV. The Te surface state shows up as a much more intense feature in the ARPES below $-500$ meV, with an expected dispersion and flanked at the lower energy side by bulklike intensity. The difference in intensity between the surface states and the bulk bands in the EDM can be explained by taking into consideration that, for a photon energy of 21.2 eV, the escape depth of the emitted electron is of the order of only a couple of nm. This means that we expect the surface states with large weight on the outermost Te atomic layer to be more intense than those with large weight on the Bi/Sb layer beneath. Moreover, we also expect these surface states to be more intense than the bulklike states from the layers below, even though the latter are greater in number. In particular, we observe that the Te surface state is asymmetrically sensitive to the $p$-polarized light, while the bulklike states and the TSS are more symmetric. A more detailed description is provided in the SM.

The location of the DP, $E_D$, with respect to the top of the VB, along $K - \Gamma - K$, as found in the TB calculations is slightly different than observed in ARPES. From the ARPES EDM, we find the DP to lie approximately 50 meV above the top of the VB, whereas in the TB slab calculation $E_D$ coincides with the top of the bunched VB bulk states in the $\Gamma - K$ direction. By extracting the Dirac fermion velocity from the linear dispersion around the DP from the ARPES EDM, using an undistorted upper cone fitted to the $\bar{K} - \bar{K}$ dispersion angle, we find $v_F$ to be about $4.7 \times 10^5$ m/s. By applying the same procedure on the TB-calculated TSS dispersion, we find a $v_F$ of $4.1 \times 10^5$ m/s, which closely resembles the experimental value. Additionally, these values are also in good correspondence with previously published calculations [27] and ARPES data [4]. However, in the TB slab calculations, we note that at energies just below $E_D$, the TSS present a flat-band behavior, causing them to exhibit a nonlinear behavior at energies close to the VB.

**B. Scanning tunneling spectroscopy**

The subband spacing in Sb$_2$Te$_3$ determined by quantum confinement was previously shown to give rise to weak oscillations in the DOS, as revealed by STS [16]. The quantum well states were shown to vary with the thickness of the slab. We anticipate that the situation is very different for (Bi$_{1-x}$Sb)$_2$Te$_3$: the bunched nature of the quantum well states should give a strong signal in STS and the peak positions are mainly given by the energies where the bands are flat. In (Bi$_{0.5}$Sb$_{0.6}$)$_2$Te$_3$, this bunching effect of flat bands turns out to occur, at comparable $E - E_F$, independent of the slab thickness, see Fig. S1.

STS data can, in some cases, also provide information on the dispersion of the energy bands [29], as elucidated in the SM. We show that the extracted Fermi velocity, $v_F$, from the voltage dependence of the inverse decay length in the vicinity of the DP gives a $v_F$ of about $1.5 \times 10^5$ m/s. Note that this value is significantly lower than the $v_F$ extracted from the ARPES EDM, because the latter $v_F$ was extracted higher up in the cone. This is in excellent agreement with the approximately $2.4 \times 10^5$ m/s found using our TB model by considering the apex to be at $-0.15$ eV relative to $E_F$, and the tangent to the DP.

We use the Tersoff-Hamann model to simulate the tunnel currents using the LDOS derived from our TB model [23]. This way, we are able to resolve the contribution of the electronic bands to the total $dl/dV$ of an STS spectrum. The band structure for a free-standing six-QL (Bi$_{0.5}$Sb$_{0.6}$)$_2$Te$_3$ film is presented in Fig. 4(a). The resulting simulation of
the corresponding STS spectrum is shown in Fig. 4(b). The $k_z$-dependent decay length of the states into the vacuum will cause the STS to be most sensitive to the dispersions close to the $\Gamma$ point and, in particular, to the ones giving rise to van Hove singularities. This is clearly observed in the computed normalized $dl/dV$ curves in Fig. 4(b). Our TB calculations reveal that the LDOS in the VB is dominated by a Te surface state contribution whose location and character is unchanged on altering the thickness, as can be seen in Fig. S1, and to variation in the alloy fraction.

The STS measurement of a 5-nm-thin (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ film in Fig. 4(c) shows all the important features that can also be recognized in the TB calculations presented in Figs. 4(a) and 4(b). In the TB calculation, $E_F$ is locked to the top of the bulk VB around M/6. The recorded STS spectrum, however, reveals that, experimentally, $E_F$ tends to shift to the bottom of the conduction band. In the SM, an additional STS measurement is presented, which was performed on another 5-nm-thin (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ film and shows the same weak oscillations in the DOS with a similar peak separation, but with the $E_F$ at a different position, see Fig. S3. This discrepancy of the location of the $E_F$ observed when comparing the results from Fig. S3 with those presented in the main text is more frequently observed when comparing individual spectroscopy results from sample to sample, and even when comparing different terraces on a single sample. This variation can be attributed to either the adsorption process of molecules to the film surface or the presence of defects in the material, such as Te vacancies. To present an estimate of the shift of the $E_F$ that can be induced in the material by Te vacancies, we first make the assumption that $E_F$ is located within the bulk band gap and only crosses the TSS, characterized by a linear dispersion with $v_F = 4.7 \times 10^5$ m/s. For this dispersion, a shift of 100 meV is accompanied by a wave vector change of about 0.15 eV for the comparison in EF. Our TB approach, and the spectroscopy experiments provide an adequate and complete picture of the electronic properties of our material system.

**IV. CONCLUSION**

In summary, the TB modeling shows that the bunching of bulk subbands in the alloy (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ is likely caused by a Sb/Bi substitution induced change in band order, close to $E_F$ near $\Gamma$, with the TSS still separated from the VB. The fact that the DP lies in close proximity to the bunched bulk subbands, which are vulnerable to alloy disorder, makes this material system the perfect platform to investigate the robustness of the TSS against disorder. The close correlations between the TB slab calculations and ARPES measurements allow us to elaborate on the atomic origin of electronic bands near $E_F$, providing a good understanding of the electronic structure of an alloy of the TI (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$. By combining the results acquired in the spectroscopy experiments and TB calculations we are able to attribute the oscillatory behavior of the DOS in the STS measurements, performed on 5 nm (Bi$_{0.4}$Sb$_{0.6}$)$_2$Te$_3$ films, to the flat bunching states with a bulk character and to the Van Hove singularity of the Te surface state in the VB.

This detailed understanding of the material system will allow for future experiments in the direction of even thinner slabs where a hybridization gap will be induced in the TSS. Devices can be equipped with a gate to tune into the hybridization gap that occurs at the DP, hereby enabling access to the topological edge states. The spectroscopy measurements confirmed that the DP is in close proximity to the bulk VB. Therefore, to observe signatures of a possible QSH state, for example, via magneto-transport measurements, the stoichiometry still shows some room for further optimization. We present Sb$_2$Te$_3$ as another possible candidate to perform future research to the QSH state of matter.

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Since we found that the location of the subbands is rather invariant upon changing the film thickness, we are also able to state that the STS measurement matches the results from our ARPES study, presented in Fig. 3(a). Therefore, we can state that the combination of our theoretically predicted electronic structure, using a TB approach, and the spectroscopy experiments provides an adequate and complete picture of the electronic properties of our material system.


