Bulk and surface electron dynamics in a $p$-type topological insulator SnSb$_2$Te$_4$

D. Niesner,¹ S. Otto,¹ V. Hermann,¹ Th. Fauster,¹ T. V. Menshikov,² S. V. Eremeev,²,³ Z. S. Aliev,⁴ I. R. Amiraslanov,⁴,⁵ M. B. Babanly,⁴ P. M. Echenique,⁶ and E. V. Chulkov⁴,²

¹Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany
²Tomsk State University, pr. Leningrad 26, 634050 Tomsk, Russia
³Institute of Strength Physics and Materials Science SB RAS, pr. Akademicheskiy 2/4, 634021 Tomsk, Russia
⁴Baku State University, General and Inorganic Chemistry Department, Baku, Azerbaijan
⁵Institute of Physics, Azerbaijan National Academy of Science, Baku, Azerbaijan
⁶Donostia International Physics Center (DIPC), Departamento de Física de Materiales and CFM-MPC UPV/EHU, 20080 San Sebastian, Spain

(Received 11 September 2013; revised manuscript received 16 January 2014; published 14 February 2014)

Time-resolved two-photon photoemission was used to study the electronic structure and dynamics at the surface of SnSb$_2$Te$_4$, a $p$-type topological insulator. The Dirac point is found 0.32 ± 0.03 eV above the Fermi level. Electrons from the conduction band minimum are scattered on a time scale of 43 ± 4 fs to the Dirac cone. From there they decay to the partly depleted valence band with a time constant of 78 ± 5 fs. The significant interaction of the Dirac states with bulk bands is attributed to their bulk penetration depth of ~3 nm as found from density functional theory calculations.

DOI: 10.1103/PhysRevB.89.081404

While topological insulators (TIs) are bulk insulators, they exhibit a spin-polarized metallic topological surface state (TSS) with linear dispersion (Dirac cone) [1,2]. The helical spin structure of the Dirac cone was predicted to constrain intraband scattering in the absence of spin-flipping events, resulting in long carrier lifetimes [3]. Evidence for the suppression of elastic spin-flipping scattering events was given by Fourier-transformed scanning tunneling spectroscopy [4]. Time-resolved photoemission measures the transient population of initially empty electronic states following an optical pump pulse, and therefore allows us to access electron dynamics directly in the time domain. Previous studies have focused on carrier cooling in bismuth chalcogenides which are intrinsically $n$ type [5–7] and can be $p$ doped by Mg [8]. These studies showed that the electron dynamics of TSSs is dominated by the bulk conduction band, but did not provide scattering rates between TSS and the conduction or valence band. Such information could be related to results obtained from transport measurements and would be important for device applications.

Complex ternary Sb$_2$Te$_3$-based alloys possess a layer structure with a van der Waals gap between Te layers and were recently proposed to exhibit a topological surface state [9–11]. While topological insulators (TIs) are bulk insulators, they exhibit a spin-polarized metallic topological surface state (TSS) with linear dispersion (Dirac cone) [1,2]. The helical spin structure of the Dirac cone was predicted to constrain intraband scattering in the absence of spin-flipping events, resulting in long carrier lifetimes [3]. Evidence for the suppression of elastic spin-flipping scattering events was given by Fourier-transformed scanning tunneling spectroscopy [4]. Time-resolved photoemission measures the transient population of initially empty electronic states following an optical pump pulse, and therefore allows us to access electron dynamics directly in the time domain. Previous studies have focused on carrier cooling in bismuth chalcogenides which are intrinsically $n$ type [5–7] and can be $p$ doped by Mg [8]. These studies showed that the electron dynamics of TSSs is dominated by the bulk conduction band, but did not provide scattering rates between TSS and the conduction or valence band. Such information could be related to results obtained from transport measurements and would be important for device applications.

Complex ternary Sb$_2$Te$_3$-based alloys possess a layer structure with a van der Waals gap between Te layers and were recently proposed to exhibit a topological surface state [9–11]. However, intrinsic $p$ doping of antimony-containing materials does not permit to access the Dirac point by conventional angle-resolved photoelectron spectroscopy [12] even after doping by alkali-metal atoms [13]. Angle-resolved two-photon photoemission (2PPE) uses a pump-probe process to access the unoccupied electronic states as indicated by the arrows in Fig. 1(a). Here, we show that SnSb$_2$Te$_4$ is a $p$-doped TI and obtain energy and dispersion of the TSS as well as bulk conduction and valence bands by 2PPE. The results agree very well with results from density functional theory (DFT) calculations. Time-resolved 2PPE is used to measure the transient population dynamics. It is dominated by refilling from the conduction band and scattering to the valence band, which is partly depleted at the present doping level. The strong interaction between bulk and surface is attributed to the large penetration depth of the TSS.

Two-photon photoemission experiments used the fundamental (1.63 eV, IR pump) and the third harmonic (4.89 eV, UV probe) of a Ti:sapphire oscillator with a repetition rate of 90 MHz. The width of the cross-correlation trace of the two pulses is 69 fs. The laser beams are $p$ polarized and incident onto the sample under an angle of 45°. Spectra were recorded using a hemispherical analyzer (Omicron EA300HR with seven channeltrons) with an angular resolution of 1.6° and its energy resolution set to 34 meV (17 meV for high-resolution measurements). The sample azimuth was orientated monitoring the angular photoelectron distribution, ensuring that the plane of measurements matched the Dirac point within less than 1° corresponding to $\leq 0.005$ Å$^{-1}$ at a kinetic energy of 0.35 eV. The base pressure during measurements was below 2 $\times 10^{-9}$ Pa. For details of the setup, see Ref. [14].

Single-crystalline SnSb$_2$Te$_4$ was grown from melt by the vertical Bridgman-Stockbarger method. The polycrystalline SnSb$_2$Te$_4$ was placed in a conical-bottom quartz ampoule, which was sealed under a vacuum better than 10$^{-5}$ Pa. Before the growth process, the ampoule was held in the “hot” zone ($\sim 950$ K) of a two-zone tube furnace for 12 h for a complete melting of the compound. Then, the charged ampoule was moved to the “cold” zone (780 K) with 1.0 mm/h. In this way, an easy-to-cleave layered single crystal with average dimensions of 2 cm in length and 0.8 cm in diameter was obtained. The grown crystal was checked by x-ray diffraction [15] and the unit-cell parameters are in good agreement with the values given in Ref. [16]. Samples were cleaved at room temperature at a base pressure below 5 $\times 10^{-7}$ Pa and transferred to ultrahigh vacuum within a few minutes, where they were cooled within $\approx 20$ min to 90 K for measurements. Low-energy electron diffraction showed sharp spots with threefold symmetry.

For electronic band calculations, we use the Vienna $ab$ initio simulation package [17,18] with generalized gradient
The calculations show that 2PPE on SnSb₂Te₄ and on other layered compounds [24] is dominated by intermediate states, and occupied initial states do not contribute. The IPS is found in the DFT calculation even though the asymptotic Coulomb potential has not been included in the computation [25]. The state has a parabolic free-electron-like dispersion and is mostly localized in the vacuum region. These findings agree with the observations for bismuth chalcogenides [8,24]. The calculations show at $\Gamma$ two narrow bands at 2.4 and 3.1 eV [Fig. 1(a)]. Such features are absent in the spectrum of quintuple-layer-structured topological insulators of Bi₂Se₃ type and arise in the SL-structured SnSb₂Te₄ owing to the third element (Sn) in the central layer: The lower band at $\approx 2.4$ eV is composed of Sn $p_{xy}$ states, and the higher one at $\approx 3.1$ eV is mainly determined by the Sn and inner Te atom states of $p_z$ symmetry. Attempts to find these states by UV-UV 2PPE were not successful.

High-resolution 2PPE data around the bulk band gap are presented in Fig. 1(d) [23]. To enhance the relevant peak structures, we show the second derivative $-\partial^2 E_{\theta} \partial E^2$ using a color scale suppressing negative values. The linearly dispersing features cross at 0.32 eV and have a group velocity of 3.4 ± 0.3 eV Å⁻¹. They are attributed to the TSS found in other topological insulators [24,26,27]. The second spin-polarized surface state could not be confirmed by the present experiments on SnSb₂Te₄ due to overlap with the IPS emission.

The state has a parabolic free-electron-like dispersion and is mostly localized in the vacuum region. These findings agree with the observations for bismuth chalcogenides [8,24]. The calculations show at $\Gamma$ two narrow bands at 2.4 and 3.1 eV [Fig. 1(a)]. Such features are absent in the spectrum of quintuple-layer-structured topological insulators of Bi₂Se₃ type and arise in the SL-structured SnSb₂Te₄ owing to the third element (Sn) in the central layer: The lower band at $\approx 2.4$ eV is composed of Sn $p_{xy}$ states, and the higher one at $\approx 3.1$ eV is mainly determined by the Sn and inner Te atom states of $p_z$ symmetry. Attempts to find these states by UV-UV 2PPE were not successful.

High-resolution 2PPE data around the bulk band gap are presented in Fig. 1(d) [23]. To enhance the relevant peak structures, we show the second derivative $-\partial^2 E_{\theta} \partial E^2$ using a color scale suppressing negative values. The linearly dispersing features cross at 0.32 eV and have a group velocity of 3.4 ± 0.3 eV Å⁻¹. They are attributed to the TSS found in other topological insulators [24,26,27]. The second spin-polarized surface state could not be confirmed by the present experiments on SnSb₂Te₄ due to overlap with the IPS emission.

The state has a parabolic free-electron-like dispersion and is mostly localized in the vacuum region. These findings agree with the observations for bismuth chalcogenides [8,24]. The calculations show at $\Gamma$ two narrow bands at 2.4 and 3.1 eV [Fig. 1(a)]. Such features are absent in the spectrum of quintuple-layer-structured topological insulators of Bi₂Se₃ type and arise in the SL-structured SnSb₂Te₄ owing to the third element (Sn) in the central layer: The lower band at $\approx 2.4$ eV is composed of Sn $p_{xy}$ states, and the higher one at $\approx 3.1$ eV is mainly determined by the Sn and inner Te atom states of $p_z$ symmetry. Attempts to find these states by UV-UV 2PPE were not successful.

High-resolution 2PPE data around the bulk band gap are presented in Fig. 1(d) [23]. To enhance the relevant peak structures, we show the second derivative $-\partial^2 E_{\theta} \partial E^2$ using a color scale suppressing negative values. The linearly dispersing features cross at 0.32 eV and have a group velocity of 3.4 ± 0.3 eV Å⁻¹. They are attributed to the TSS found in other topological insulators [24,26,27]. The second spin-polarized surface state could not be confirmed by the present experiments on SnSb₂Te₄ due to overlap with the IPS emission.
The temporal evolution of the transient population of the states at \( \Gamma \) excited by the IR pulse is illustrated in Fig. 2. The feature at \( E_{\text{kin}} = 0.85 \text{ eV} \) [see also Fig. 1(b)] is attributed to the IPS. It shows a decay towards negative delay time indicating a UV-pump process with a lifetime of \( 17 \pm 4 \text{ fs} \). In the following, we will focus on the IR-pumped states at \( E_{\text{kin}} \leq 0.85 \text{ eV} \), i.e., \( E - E_F \leq 0.9 \text{ eV} \). The topological surface state, the first two conduction bands, and the valence band are observed within this energy window. Initially, an energetically broad electron distribution is excited in the conduction bands, which relaxes towards the conduction band minimum (CBM) with a time constant of \( \sim 240 \text{ fs} \). The time evolution of the TSS trails the one of the CBM, indicating that it is significantly populated by refilling from the CBM.

At fixed energy, the population decay directly reflects the lifetimes and decay rates. As a result, we observe single scattering events at these delays rather than the dynamics of a hot electron gas, which most previous studies on electron scattering events at these delays rather than the dynamics of the CBM. Note that for filling from higher-lying states with rate \( \Gamma_1^* \) the total decay \( \Gamma_1^* \) for filling the next lower-lying state unless other sources contribute. We discretize the CB into states \( 50 \text{ meV} \) apart, so the \( i \)-th state is located at an energy \( i \times 50 \text{ meV} \) above the CBM. The index \( i \) runs from 0 (=CBM) to 9 (\( n_{10} = 0 \)). Index \( i = 1 \) is used for the TSS below the CBM. Note that \( \Gamma_1^* \) and \( \Gamma_1 \) are effective rates including scattering from and to states in the whole Brillouin zone. Figure 3(b) illustrates the model. The data (horizontal cuts of Fig. 2 summed over 50-meV energy range) are shown in Fig. 3(a) together with fits using Eq. (1). Additional measurements using smaller delay steps are given for CBM and TSS [lower panel of Fig. 3(a)]. A fit of Eq. (1) to the time-resolved spectrum of the TSS using the experimental CBM occupation \( n_0 \) as a source term yields lifetimes of \( 43 \pm 4 \text{ fs} \) for the CBM and \( 78 \pm 5 \text{ fs} \) for the TSS [squares in Fig. 3(c)].

The scattering rates resulting from the fits using Eq. (1) to the complete data set of Fig. 3(a) are shown in Fig. 3(c). The different values obtained for the CBM and TSS from the time-resolved data in the bottom panel are due to sample degradation during the time to collect the series of energy spectra in the top panel subsequently. For most energies, the rates \( \Gamma_1 \) and \( \Gamma_1^* \) agree, indicating a decay within the conduction band. An exception occurs for \( \Gamma_1^* > \Gamma_1 \), which can be explained by filling of the CBM by electrons from \( k_{\|} \neq 0 \) or from the subsurface region. Within the second conduction band CB2, \( \Gamma_1^* \) is quite small, indicating scattering to other bands or states with \( k_{\|} = 0 \). This might be related to the negative dispersion of CB2. In general, the decay rates decrease with decreasing energy in the CBs. At the CBM, the decay rate is a factor 3 larger than at 50-meV higher energy. We attribute this to quasielastic scattering (by phonons or defects) from the CBM to the TSS which is supported by the close similarity between the time-resolved spectra of the CBM and the TSS. Note that the TSS is split off from the band edges and has a wave function derived from VBM and CBM states. The occupation of the TSS decays with a time constant of 78 fs into VB states. For a higher-doped surface \( (E_{\text{VBM}} - E_F = 0.42 \text{ eV}) \) we find a lifetime of \( 45 \pm 4 \text{ fs} \) due to the additional VB states available for decay at higher-doped \( p \)-type surfaces [28]. Within the experimental error of \( \pm 4 \text{ fs} \), the lifetime along the TSS band is constant for \( |k_{\|}| < 0.025 \text{ Å}^{-1} \) [28]. The lifetimes \( \tau \) scale within the experimental uncertainties as \( \tau \propto E_{\text{VBM}}^{-1} \). The energy \( E_{\text{VBM}} \) of the VBM above \( E_F \) determines the phase space for inelastic decay of the TSS and is taken as 0.18 eV [from calculations in Fig. 1(e)] below the experimental CBM.

As a result of the helical spin structure of the TSS, long lifetimes of carriers excited into this state may be expected. The \( GW \) approximation calculations of intraband decay in the Dirac state of Bi$_2$Se$_3$ predict a lifetime of \( \sim 1 \text{ ps} \) [3]. In contrast, for SnSb$_2$Te$_4$, where the Fermi level is located 0.3 eV below the Dirac point, we find a relatively short lifetime of only 78 fs. This can be attributed to scattering from the TSS.
to the bulk VB. A lifetime of 6 ps has been reported for $p$-type-doped Bi$_2$Se$_3$ with a Fermi level position $\approx 70$ meV below the Dirac point [8] and attributed to filling from the CB. In Bi$_2$Se$_3$, the top of the VB is located at 50 meV below the Dirac point [29], i.e., $E_{\text{VBM}} \approx 20$ meV. The $\tau \propto E_{\text{VBM}}^{-2}$ scaling used for SnSb$_2$Te$_4$ would yield a lifetime for Bi$_2$Se$_3$ of 3 ps similar to the theoretically predicted intraband decay rate [3] but significantly shorter than the dominating lifetime of the CB.

The scattering time from the CBM to the TSS is also quite short (43 fs). This scattering proceeds quasielastically and is followed by downward relaxation along the TSS [Fig. 3(b)]. The strong coupling between bulk CB and VB to the TSS can be explained by the sizable penetration depth of the Dirac state of two structural units [25] similar to quintuple-layered materials such as Bi$_2$Se$_3$ [30]. For SnSb$_2$Te$_4$, the penetration is $\sim 30$ Å and leads to an enhanced scattering from or to bulk states.

The valence band is included in rate-equation model (1) only indirectly as a channel at lower energy into which the TSS electrons decay. The immediate increase of the VB intensity shown in Fig. 2 indicates that the VB is populated only indirectly as a channel at lower energy into which the states.

The authors thank I. A. Nechaev for helpful discussions. We acknowledge partial support from the Basque Country Government, Departamento de Educación, Universidades e Investigación (Grant No. IT-366-07), the Spanish Ministerio de Ciencia e Innovación (Grant No. FIS2010-19609-C02-00), the Ministry of Education and Science of Russian Federation (Grant No. 2.8575.2013), the Russian Foundation for Basic Research (Grant No. 13-02-12110 _oh_m), and Science Development Foundation under the President of the Republic of Azerbaijan [Grant No. EIF-2011-1(3)-82/69/4-M-50].

References

[14] A Bruker D8 ADVANCE diffractometer with Cu–Kα radiation was used. The unit-cell parameters were calculated with EVA and TOPAS V3.0 software.

[23] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.081404 for original spectra of Figs. 1(a) and 1(d). All data were recorded after reaching a stable level of the work function. The value after cleaving and transferring the sample to the spectrometer is above 5.5 eV and decreases within an hour to a stationary level around 5.0 eV. Likewise, the energy of the Dirac point varies slightly. A similar behavior is found for bismuth chalcogenides [24].


[25] See Ref. [23] for probability densities of IPS and TSS.


[31] See Ref. [23] for details of the fitting procedure.

