Switching on surface conduction in a topological insulator

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(Dated: October 22, 2020)

Abstract

The protected surface conductivity of topological insulators, carried by ultra-relativistic Dirac fermions, is in high demand for the next generation of electronic devices. Progress in the unambiguous identification of this surface contribution and, in a second step, its control are needed to move forward. Here we demonstrate both, with a combined transport and spectroscopy study of high-quality single crystals and mesoscopic devices of the topological insulator TlBiSe2−δ. We show how various external stimuli—from thermal radiation, via low-intensity light, to high-intensity laser pumping and current driving—can boost the surface contribution, thereby making it both unambiguously detectable and potentially exploitable for applications. Once switched on, the extra surface contribution is persistent, with lifetimes of hundreds of years at low temperatures. We understand this effect in terms of the well-known concept of surface charge accumulation via a Schottky barrier formation, and propose that the same mechanism underlies also the slow relaxations seen with spectroscopic probes in our and other materials, which might thus also be persistent. We expect our technique to be readily transferable to other materials and probes, thereby shedding light on unexplained slow relaxations in transport and beyond.

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Three-dimensional topological insulators are considered as promising candidates for the next generation of electronic devices\textsuperscript{20}. However, initial high expectations of fast success were toned down as challenges to realize such devices became apparent. For instance, contributions of bulk states frequently hinder an unambiguous identification of topological surface conduction, and thus of its control and exploitation. To minimize bulk carrier effects, studies are performed at low temperatures, as function of doping\textsuperscript{8,21}, electrostatic\textsuperscript{22,23}, or optical gating\textsuperscript{24,25}, some of these techniques being limited to nanometric samples. Simple methods for the \textit{in-situ} control of topological surface conduction, that are broadly applicable also to bulk samples, are yet to be discovered. This is what we do in the present work.

We have performed an electrical transport study of the bulk three-dimensional topological insulator $\text{Tl}_{1-x}\text{Bi}_{1+x}\text{Se}_{2-\delta}$ (Fig. 1\textit{a}). The material with $x = 0.025$ (referred to as “bulk-insulating”) provides ideal starting conditions: an isolated surface Dirac point situated in the band gap of the bulk states, and great tunability of the Fermi level by changing the off-stoichiometry via the variation of $x$\textsuperscript{26,27}. This is seen in angle-resolved photoemission spectroscopy (ARPES) as an energy shift of the Fermi level with $x$ (Fig. 1\textit{b}), and in electrical resistivity measurements as orders of magnitude variation of the low-temperature resistivity with $x$ (Fig. 1\textit{c}). The presence of high mobility electrons (the surface Dirac electrons) and low mobility (bulk) holes is evidenced from a two-carrier analysis\textsuperscript{28,29} (Extended Data 1).

In the temperature-dependent electrical resistivity curves of samples with $x < 0.064$, we observe an anomaly at a characteristic temperature $T^* \approx 40$ K. This anomaly is also seen in the dc-susceptibility (Extended Data 2\textit{a}), but not in the specific heat (Extended Data 2\textit{b}), indicating that it is not a bulk effect (such as a bulk phase transition), but should instead be attributed to surface states. In what follows we focus on the bulk-insulating compound $x = 0.025$. Above $T^*$, its electrical resistivity obeys an Arrhenius law, with an activation energy of 28 meV (Extended Data 3\textit{b}), and its current-voltage characteristics show an extended range of quasi-linear behaviour, corresponding to normal ohmic conduction (Fig. 1\textit{f} and Extended Data 3\textit{a}). Below $T^*$, we observe striking deviations from this behaviour, which we attribute to the presence of a Schottky barrier between the Dirac surface states and the gapped bulk states\textsuperscript{30}, as sketched in Fig. 1\textit{h} (see SI 1).

Various kinds of radiation profoundly modify the transport behaviour below $T^*$. In a first set of experiments, we measured the electrical resistivity of the bulk-insulating sample during cooling to 2 K (black curve in Fig. 2\textit{a}), expose it there to illumination from a near-infrared light emitting diode (NIR LED), then switch off the LED and measure the electrical resistivity during warming.
The orange and green curves are for two such runs, with a shorter and longer illumination time, respectively, the latter being long enough to reach a steady state (i.e., longer irradiation does not lead to a further resistance change). Compared to the measurement without illumination, a strong decrease of the low-temperature electrical resistivity is observed, up to an order of magnitude at 2 K, corresponding to a large positive photoconductivity, with the size of the effect being controlled by the illumination duration.

Intriguingly, also black-body radiation affects the resistivity, which we noticed when performing an experiment without a radiation shield (see Methods). We present two experiments, one with a shortened radiation shield (leading to black-body radiation from temperatures only slightly above the sample temperature, red curve in Fig. 2a and orange points in Extended Data 4a) and one without a shield (leading to black-body radiation from room temperature, blue curve in Fig. 2a and red points in Extended Data 4a). In both cases, the sample was held at 2 K under these shielding conditions until a steady state was reached, and then measured during warming. The experiment with incomplete shielding results in a much weaker resistivity reduction than the experiment without a shield. On the other hand we see that the data from the experiments with (steady state) black-body radiation from room temperature and NIR radiation from the LED (blue and green curves in Fig. 2a, respectively) almost collapse.

Before proceeding, we note on several points. Firstly, the sensitivity to even spurious thermal radiation explains the anomalies at $T^*$ in the resistivity curves taken without intentional illumination (black, red, and orange curves in Fig. 1c and black curve in Fig. 2a). Secondly, the effect is fully reversible by heating the sample above $T^*$. This excludes surface pollution and sample ageing effects as origins. And thirdly, the effect is seen after the illumination is switched off. Thus, the photoexcited carriers have a lifetime that is, at least, long on the time scale of the resistivity measurement.

To explore the relaxation behaviour further, we measured the electrical resistivity at several fixed temperatures as function of time, both during illumination with the NIR LED ($0 < t < 7200$ s) and after switching it off ($t > 7200$ s, Fig. 2c). At high temperatures, the relaxation is fast on the time scales of our measurements (about 1 s) but with decreasing temperature an increasingly slow relaxation is observed (spurious heating effects are discussed in Extended Data 5). Most striking is the effect that when switching the LED off after having reached the equilibrium state at 2 K, the resistivity barely evolves on the time scale of our experiment (see lowest temperature curve in Fig. 2c). This is the phenomenon of persistent photoconductivity.
We also analyse the time dependence quantitatively. The relaxation after switching the LED off follows a stretched-exponential relaxation \[ R \propto \exp \left[ -\left( \frac{t}{\tau} \right)^n \right] \] (with \( n < 1 \)), as shown by the black lines in Fig. 2c (with the condition \( R_{t \to \infty} = R_{t<0} \) during relaxation). The temperature dependence of the relaxation time \( \tau \) is shown in Fig. 2d. It increases by almost 9 orders of magnitude as temperature is only slightly reduced, from 35 to 20 K, before saturating at lower temperatures. Above 20 K, this temperature dependence can be approximated by a thermal activation law, \( \ln(\tau) \propto E_B/k_B T \), with \( E_B \approx 82 \) meV, interpreted as the Schottky barrier height. From this dependence we derive that, below 20 K, a relaxation of the resistivity to 90% of its initial value before irradiation would take hundreds of years—persistence par excellence (see Extended Data 5).

Next we show that the surface conductivity can also be tuned using electrical currents. Applying a large current at low temperatures leads to a controlled and permanent decrease of the resistivity which, analogous to the illumination experiments, is measured upon warming, after reducing the large tuning current to a small measurement current of 10 \( \mu \)A to exclude overheating (Fig. 2b). Again, the effect is reversible by heating the sample above \( T^* \).

This current-induced decrease of the resistivity below \( T^* \) is visible in the current-voltage characteristics as a memory effect. In the 2 K isotherm (Fig. 1e), a hysteresis is observed between the increasing-current curve (from 0 to 50 mA) and the decreasing-current curve (from 50 mA back to 0) but, interestingly, not between the subsequent up and down sweeps with negative applied current. The hysteresis can thus be attributed to the current-induced switching from the initial high-resistance state (black line in Fig. 2b) to the low-resistance state (purple triangles). Once the sample has switched, it remains in the low-resistance state until it is heated above \( T^* \). Thus, no hysteresis appears under negative currents, and not under positive currents in a second loop either. The characteristic time of the current-induced resistivity change is much faster than that of the illumination-induced process; in fact, it is smaller than the typical time scale of our measurements (about 1 s) and could thus not be resolved.

How can we understand the salient features observed in all these experiments in a consistent way? From the similarities between the light-induced and electrical current-driven reduction of the resistivity, a common mechanism is expected and therefore both purely optical \(^{19,24}\) and purely electric-field-induced effects \(^{17,33,34}\) are excluded.

We first address the effects induced by the NIR radiation, i.e., the large positive and persistent photoconductivity with stretched-exponential relaxation. NIR light penetrates 0.16 – 1 \( \mu \)m into
the sample—much deeper than the depletion depth $W$ (around 15 nm, see Methods)—and has
sufficient energy ($\approx 1.25 \text{ eV}$) to excite carriers across the bulk band gap ($\geq 0.3 \text{ eV}$ [5]). Thus,
we propose that electrons, photoexcited across the bulk band gap, migrate to the surface due to
the downward band bending associated with the Schottky barrier, and populate the Dirac surface
states (as sketched in Fig. 2e, top). This creates a surface charge accumulation with space-charge
separation between the Dirac electrons and the bulk holes. By populating the Dirac states, the
barrier height $E_B$ and, as a consequence, the depletion width $W$ (see Eq. 1 in the Methods)
decrease. This description is supported by Hall effect experiments. They reveal a pronounced
illumination-induced change of the Hall coefficient below $T^*$ (Extended Data 1) which, in an ex-
tended two-carrier analysis, is associated with an increase of the surface carrier concentration (see
SI II). The stretched-exponential decay is understood as follows: the photoexcited Dirac electrons
on the surface are separated from the photoexcited holes in the bulk by the Schottky barrier. At
low temperatures, the recombination process is dominated by tunnelling across the depleted area
(as sketched in Fig. 2e, bottom). The barrier height $E_B$ and depletion width $W$ increase as the
Dirac states are depopulated. As a consequence, the tunnelling rate decreases with time during
relaxation, compatible with the stretched-exponential decay.

We now turn to the sensitivity to spurious black-body radiation. The power density from a
black body at 300 K is centered at 155 meV (8 $\mu$m) with a significant part of the distribution
above 300 meV, which is large enough to excite carriers across the energy gap. The steady-
state photoconductivity from this radiation is almost identical to the one from the much higher
energy NIR LED (blue and green curves in Fig. 2a, respectively). This shows that, as long as
the radiation has sufficient energy to excite carriers across the energy gap, a unique steady-state
conductivity is reached. This is strong support for the conductivity in the irradiated state being
dominated by surface conduction because the different energy ranges of the two types of radi-
ations imply different penetration depths into the sample. If this resistivity reduction were due
to (metastable) bulk carriers (for instance involving deep impurity centres [35]), different portions
of the bulk sample would contribute and thus different saturation resistivities would be observed.
By contrast, black-body radiation from much lower temperature as expected from the shortened
radiation shield has insufficient energy to excite carriers across the bulk gap. However, because
bulk-insulating Tl$_{1-x}$Bi$_{1+x}$Se$_{2-\delta}$ is slightly off-stoichiometric, there may be shallow in-gap states
with trapped carriers, and these might be photoexcited to the bulk conduction (or valence) band.
This can explain the weaker resistivity reduction of the curve with partial shielding (red curve in
Next we discuss the electrical current-driven effect. As shown above, there is a current threshold (between 10 and 15 mA, Fig. 1e, see also Extended Data 3) for low-temperature resistance switching to occur. For currents (and corresponding electrical fields) above this threshold, the bulk conduction band is partially populated by electrons via electric field injection (see SI 1). At low temperatures, these electrons then lead to “current-conductivity”, analogous to the photoconductivity under irradiation.

We now present photocontrol studies on micrometric samples, fabricated with the focused-ion beam (FIB) cutting technique (Fig. 3a). The temperature-dependent resistances of two such samples again show a pronounced drop below about 40 K when illuminated (Fig. 3b), and the time dependence upon illumination again follows stretched-exponential behaviour (Fig. 3c). Both this qualitative similarity to the results on the bulk sample and two quantitative differences, reported next, lend further support to our interpretation, and confirm the only minor contribution of bulk conduction. Firstly, during illumination, the saturation resistance is reached in only a few minutes instead of a few hours, which we attribute to the light penetration depth being similar to or larger than the thickness of the sample (0.16 − 1 µm and 0.3 µm, respectively, see Methods), and thus the irradiation hitting the entire volume of the sample at once. Secondly, the resistance under illumination is lower at low temperature than it is at room temperature (ratio $R/R_{300\,\text{K}} < 1$), which we understand as caused by a much larger relative contribution of the surface conduction in the samples. Our results demonstrate the robustness of the photocontrol of Dirac surface conduction against microfabrication, thus paving the way for device applications.

Finally we studied the Dirac surface states with time-resolved ARPES (tr-ARPES) experiments. In the bulk-insulating sample ($x = 0.025$), after pumping, a shift of the (quasi-)Fermi level by 93 meV is observed and persists for at least 4 µs (Fig. 4a, c and Extended Data 6a, c). This shift is composed of an actual shift of the Fermi level on the surface by $\delta_E = 28$ meV—caused by the filling of the Dirac states upon pumping (Figs. 4f-h)—and of a shift by $\Delta_E = 65$ meV caused by a surface photovoltage due to a relaxation of the band bending (Fig. 4g). To visualize the charge accumulation at the surface more directly, we subtract the spectrum without pump but shifted by 65 meV (Fig. 4b) from the spectrum taken 4 µs after the pump (Fig. 4c). The difference spectrum (Fig. 4d) as well as the difference of the angle-integrated intensity (Fig. 4e) clearly reveal extra charge corresponding to a Fermi level shift of 28 meV. No such “persistent” shift of the Fermi level is detected in the bulk-metallic sample (Extended Data 6b, d). In addition, very different
relaxation times of the excited states between both samples are found (Extended Data 6). Only if the Fermi level is situated inside the bulk band gap, we observe a slow (≥ 4 μs) relaxation, similar to that observed in other topological insulators\textsuperscript{11–16}. Our accompanying transport study on the same material allows us to relate this “more-than-4 μs-long” relaxation to an ultraslow “more-than-hour-long” relaxation. We conjecture that the underlying mechanism is the same and that, thus, also the tr-ARPES pump induces a state of persistent topological surface conduction in bulk insulating Tl\textsubscript{1−x}Bi\textsubscript{1+x}Se\textsubscript{2−δ} (x = 0.025).

We expect our work to have broad implications. Firstly, we have put forward experiments with readily accessible “pumping”—weak light/radiation or electrical current—which lend themselves for experiments also on other samples in many laboratories worldwide, as well as for implementation in experiments beyond transport. An interesting candidate for such future studies is for instance the putative topological Kondo insulator SmB\textsubscript{6}\textsuperscript{10}. Secondly, because of the persistence of the surface conduction, the “pump” can be switched off after the surface charge is generated. This will avoid any interferences with it both in fundamental studies and future device applications. And finally, the control does not rely on the presence of defect or impurity states and is even robust against rather harsh microstructuring techniques, ensuring reliability.


FIG. 1: Characterization of Tl$_{1-x}$Bi$_{1+x}$Se$_{2-\delta}$ single crystals. a: Crystal structure forming Tl-Se-Bi-Se quadruple layers. b: ARPES measurement around the $\bar{\Gamma}$ point of the bulk-metallic ($x = 0.064$, left) and bulk-insulating sample ($x = 0.025$, right) at 7 K. c: Temperature dependence of the electrical resistivity for samples with different off-stochiometry $x$. An anomaly is visible at $T^* \approx 40$ K, independent of $x$. d: Sketch of the energy $E$ vs distance from surface $z$ without external stimulus, when the Fermi energy $E_F$ lies in the bulk band gap, showing the formation of a Schottky barrier. $W$ and $E_B$ are the depletion region and barrier height, TSS the topological surface states, and BVB and BCB the bulk valence band and the bulk conduction band, respectively. e: Current-voltage characteristics of the sample with $x = 0.025$ at selected temperatures without illumination, showing deviations from Ohm’s law due to the presence of the Schottky barrier and the development of switching and memory effects below $T^*$. The arrows indicate the measurement sequence: $0 \rightarrow 50$ mA $\rightarrow -50$ mA $\rightarrow 0$. 
FIG. 2: Tuning the surface conductivity of Tl$_{1-x}$Bi$_{1+x}$Se$_{2−δ}$ ($x = 0.025$) in transport. 

a: Photocontrol of the resistivity under different conditions. The poorer the thermal shielding (black → red → blue), the stronger the resistivity suppression below $T^*$ (see also Extended Data 4).

Intentional illumination with a NIR source (orange, green) was applied with two different exposure times at 2 K, and switched off just before the measurements were performed upon warming. All measurements were done with an excitation current of 10 µA. b: Current-control of the resistivity, with different currents applied at 2 K before the measurements, which were then performed with 10 µA upon warming. All current-controlled measurements were performed under good thermal shielding. The blue and black curves are reproduced from a for comparison.

c: Time dependence of the normalized resistance upon illumination below 40 K. The illumination is on between $t = 0$ and 7200 s, and then is switched off. The black solid lines are fits using a stretched-exponential (see text).

d: Relaxation time $\tau$ as function of temperature, reaching 317 years at 10 K.

e: Energy vs distance from surface diagrams, sketching the illumination and relaxation process. Under illumination, photoexcited electrons and holes are generated in the bulk, and migrate to the surface and bulk states, respectively, due to the downward band-bending. This leads to surface charge accumulation and space-charge separation, modifying thus the band-bending and shifting the Dirac cone accordingly. After turning off the illumination, the excited Dirac electrons recombine with the excited bulk holes, which at low temperatures can only occur via tunneling.
FIG. 3: Photoconductivity in micro-fabricated $\text{Tl}_{1-x}\text{Bi}_{1+x}\text{Se}_{2-\delta}$ ($x = 0.025$) samples. a: Scanning electron microscopy image of a typical structure with current ($I_1$ and $I_2$) and voltage ($V_1$ and $V_2$) leads. The white bar corresponds to 5 $\mu$m. b: Temperature dependence of the resistance, normalized to its value at room temperature, without and with illumination in two samples (L1 and L2). c: Time dependence upon illumination at 5 K in sample L1. A stretched-exponential relaxation is observed (red line), with an ultralong time constant of $9 \cdot 10^6$ s estimated for the relaxation process.
FIG. 4: Tr-ARPES in Tl\textsubscript{1−x}Bi\textsubscript{1+x}Se\textsubscript{2−δ} (x = 0.025) at 7 K. a-c: Dispersion of the surface states around the $\bar{\Gamma}$ point without pump (a) and after the longest possible pump-probe delay of 4µs (c). The spectrum in b corresponds to the one in a shifted by +65 meV. d: Difference between the distributions shown in b and c. e: Angle-integrated energy distribution curves of the spectra shown in a-c (top), and difference between the red and solid black curves (bottom). The interval of integration was [-14.5°, 14.5°]. f-i: Schematic of the photovoltage generated on the surface of a bulk-insulating topological insulator (see text).
Methods

Sample properties. The Tl$_{1-x}$Bi$_{1+x}$Se$_{2-\delta}$ single crystals ($\delta = 0.28$) used in this study were grown as described in Ref. 26. The bulk band gap is around 300 meV [5]. The tuning of the Fermi level by the off-stoichiometry $x$ is confirmed by ARPES and by the dependence of the resistivity on $x$ [26,27] (Figs. 1b, c). Resistivity and current-voltage characteristics give, respectively, an activation energy of around 28 and 25 meV (see SI I). The depletion depth $W$ is estimated by solving the Poisson equation, giving

$$W = \sqrt{\frac{2\epsilon_S}{e^2n}(E_B - eV - k_BT)},$$

(1)

where $\epsilon_S$ is the permittivity of the material, $e$ the elementary charge, $n$ the carrier density, $E_B$ the barrier height, $V$ the applied voltage, $k_B$ the Boltzmann constant, and $T$ the temperature. Using $n = 10^{22}$ m$^{-3}$, the permittivity $\epsilon_S = 21\epsilon_0$ [38], and $E_B = 82$ meV obtained from the temperature dependence of the relaxation time (Fig. 2d), one finds $W \approx 15$ nm at low temperatures without applied voltage. An estimate of the light penetration depths using the light source is obtained using early studies of TlBiSe$_2$ thin films [39,40], depending on the growth condition, the light penetration depth at a wavelength $\lambda = 2 \mu$m (optical response around 1 $\mu$m not reported to the best of our knowledge) varies between 0.16 and 1 $\mu$m, which is much larger than the depletion depth, therefore confirming that the light generates bulk excited carriers.

Physical properties. The resistivity was measured with spot-welded or silver-paint contacts using 10 or 25 $\mu$m diameter gold wires. Similar results were observed in different samples and with different contact configurations, highlighting the robustness of the results. The samples were obtained by cleaving a larger piece and were typically 0.5-1 mm in length and width, and 50-200 $\mu$m in thickness. The measurements were performed down to 2 K, in part in a Physical Property Measurement System (PPMS) from Quantum Design Inc. using either the standard resistivity option or the ac-resistance bridge option for the high-current measurements, and in part in an Oxford flow cryostat with a home-made setup. In the latter, a lock-in SR830, and for the current-voltage characteristics, a Keithley source meter 3624B were used. The specific heat was also measured in the PPMS. The magnetization measurements were performed with a SQUID magnetometer from Cryogenics model S700X, the illumination coming from black-body radiation due to the absence of radiation shields.

Study of the photoresponse. In the PPMS, the sample faces either the bottom of the last radiation buffer or the cap at the top of the sample chamber, depending on whether or not the radiation buffers
provided by Quantum Design Inc. were installed. Accordingly, black-body radiation comes either from the temperature of the last buffer or from room temperature. The last buffer of the radiation shield is close to the sample and its temperature is therefore expected to be only slightly higher than that of the sample. In the flow cryostat, the measurements were done with a thermal radiation shield thermally shorted to the sample holder thus having the same temperature as the sample, ensuring a minimum of spurious radiation. The light source is a commercial infrared LED from SHARP GL4800E0000F with a peak emission wavelength of 0.95 µm, situated typically 2-3 cm above the sample inside the thermal radiation shield. It is controlled with a Keithley current source 2200.

**Memory effect.** The memory effect was measured by cooling down the sample to 2 K under a permanent or shortly applied (typically a few seconds) large dc or ac current (1 to 50 mA). At low temperatures, the excitation was switched off and the resistivity was measured with a low current of 10 µA upon heating.

**Fabrication of mesoscopic samples.** We used a Quanta 200 3D dual beam system (ThermoFisher Scientific)—a gallium FIB system combined with a scanning electron microscope—to manufacture micrometric samples. Additionally, the system is equipped with micromanipulators from Kleindiek for in-chamber sample transfer.

Following a typical transmission electron microscope sample preparation recipe, a Pt protection layer of about 150 nm thickness was deposited by electron beam induced deposition to protect the near surface region of the sample. The thickness of the protection layer was increased to about 2 µm by an ion beam induced deposition (IBID) of Pt.

The preparation proceeded by removing bulk material around the protected area with the ion beam, ending up in an about 2 µm thick sample. It was freed from bulk by undercutting, followed by lifting it out, and welding it to the sample grid. In consecutive milling steps with decreasing ion currents (we used 1 nA and 500 pA for the medium thinning and 100 pA for fine milling) the thickness of the sample was reduced to about 300 nm. In order to reduce the FIB induced damage generated by the previous milling steps at 30 kV ion acceleration voltage, a final cleaning of the sample was done with 5 kV and 30 pA.

The grid with the sample was rotated by 90° and loaded together with the measuring platform to the FIB chamber. After removing the remainder of the protection layer, the sample was welded by ion beam induced tungsten deposition to the micromanipulator tip and cut off from the grid. Subsequently, the sample was transported to the measuring platform, consisting of Ti/Au stripes (5 nm/45 nm thick re-
respectively) on a SiO$_2$/Si substrate, and welded by IBID to the substrate, to stabilize the sample over the electrical contacts. The contacts were fabricated by Pt IBID with Trimethylcyclopentadienyl-platinum [(CH$_3$)$_3$CH$_3$C$_5$H$_4$Pt] as the precursor and the following ion beam parameters: acceleration voltage 30 kV, beam current 50 pA, dwell time 0.2 $\mu$s, and beam overlap 0%. The connection of the sample to the substrate was cut after contact deposition.

**Time-resolved angle-resolved photoemission spectroscopy.** The tr-ARPES apparatus consisted of a hemispherical analyzer and a mode-locked Ti:sapphire laser delivering 1.48 eV pump and 5.92 eV probe pulses at the repetition rate of 250 kHz, or at the interval of 4 $\mu$s. The energy and time resolutions were 16 meV and 300 fs, respectively. By utilizing a pin hole attached next to the sample, we estimated the spot diameters of the pump and probe beams to be 250 and 85 $\mu$m, respectively, on the sample surface and also checked that the spot of the pump beam on the sample surface did not shift within 5 $\mu$m when the delay stage in the pump beam path was shifted for 600 ps pump-probe delay. The sample was cleaved by peeling off an adhesive tape attached on the sample in the vacuum chamber at the base pressure of 5·10$^{-11}$ Torr. Measurements were performed at the temperature of 7 K.
References methods


Acknowledgements We thank Y. Ando, A. V. Balatsky, F. Libisch, S. Rotter, and M. Shiraishi for discussion, J. Baraillon and P. Hofegger for technical assistance during the measurements, and M. Schinnerl and W. Schrenk for assistance in the cleanroom. Part of this work was done in the cleanroom facilities ZMNS of TU Wien. This was been supported by the FWF grant number 29279-N27 and by KAKENHI (18H01148, 17H06138, 18H03683).


Data availability The data are available on requests to the corresponding author.

Competing interests The authors declare no competing interests.

Additional information Supplementary Information is available for this paper. Correspondence and requests for materials should be addressed to M. T. (taupin@ifp.tuwien.ac.at) or S. P. (paschen@ifp.tuwien.ac.at).
Supplementary Information

I. CURRENT-VOLTAGE CHARACTERISTICS.

A topological insulator can be naively modelled as a metal-semiconductor-metal device (the “metal” being the surface and the “semiconductor” the bulk). Charge injection from the metal to the semiconductor is frequently modelled by the relation

\[ I = I_0 (e^{\eta qV/k_B T} - 1), \]  

(2)

which captures both thermionic emission and tunnelling processes. Here \( I_0 \) is the saturation current, \( q \) the elementary charge, \( V \) the applied voltage, \( k_B \) the Boltzmann constant, \( T \) the temperature, and \( \eta \) an ideality factor.\(^3\)\(^6\) The ohmic regime at low current is taken into account by adding a linear term, giving

\[ I = I_0 (e^{\eta qV/k_B T} - 1) + V/R, \]  

(3)

where \( R \) is the resistance of the sample. With \( q = +e \) (the majority carriers being holes), our current-voltage characteristics can be rather well described by the fit, as seen by the red lines in Extended Data 3\(^a\). The activation energy \( E_A \) can be obtained through \( I_0 \) as \( \ln(I_0/T^2) \propto E_A/k_B T \) or through \( \ln R \propto E_A/2k_B T \) \( [36] \). The fact that one obtains similar activation energies in both cases (28 and 25 meV, respectively, see the blue lines in Extended Data 3\(^b\)) indicates that the model captures the situation reasonable well. The ratio of tunnelling to thermionic components is given by the ideality factor \( \eta \). Departure from unity indicates that tunnelling becomes the dominant process, as observed in our case when lowering the temperature, as shown in Extended Data 3\(^c\).

At high currents, charge injection directly into the conduction band occurs, giving an increase of the measured voltage upon illumination (shown by the arrows in Extended Data 3\(^d\)). At low temperatures, the effect of the illumination changes at the threshold current: it is reduced at small currents, and enhanced at large currents. This indicates that the switching is caused by carrier injection into the conduction band.
II. ANALYSIS OF THE HALL COEFFICIENT UNDER ILLUMINATION.

Under illumination a new conduction channel opens, namely the region of the sample into which the light penetrates. Thus, a simple two-carrier model is not applicable and an extension is needed. With the following reasonable extra assumptions one can nevertheless extract useful information. We assume that the same amount of electrons and holes is generated by the illumination, that the excited electrons migrate to the surface states (where they have the same mobility as without illumination), and that the excited holes represent the new channel and are thus allowed to have a mobility different from the bulk holes. The observed decrease of the (positive) Hall coefficient and increase of the Hall mobility (Extended Data 1) are then only feasible if these extra holes exhibit an increased mobility. This might indeed be reasonable because the original bulk holes are likely bound to in-gap states (as evidenced from the 28 meV activation energy, which is much below the intrinsic band gap of 300 meV [5]), thus adding confidence to the understanding of the transport results under illumination discussed in the main text.
Extended Data

Extended Data 1: **Photoresponse of the Hall coefficient and the Hall mobility.** a, b: Linear-response Hall coefficient $R_H$ and Hall mobility $\mu_H$ without and with illumination (black and red symbols, respectively). Without external excitation, the sheet carrier concentrations and mobilities of the bulk holes and Dirac electrons, estimated using a two-carrier analysis, are given in panels c and d, respectively. The thick lines are guides to the eyes.
Extended Data 2: **Dc-susceptibility and specific heat.** a: Temperature dependence of the volume magnetic susceptibility $\chi_{dc}$ in the bulk-insulating ($x = 0.025$) and bulk-metallic ($x = 0.064$) samples. The measurements were performed at a magnetic field of 7 T to enhance the measurement accuracy, but the same behaviour is observed at low fields. b: Temperature dependence of the specific heat in the bulk-insulating sample ($x = 0.025$).
Extended Data 3: **Current-voltage characteristics.** a: Temperature dependence of current-voltage characteristics without illumination (in fact, in our setup, we drive a current through the system and measure the voltage response); they can be described as a metal-semiconductor junction (red lines, see SI I). b: Resistance (in black, left axis) and $I_0/T^2$ (red, right axis, see SI I) versus $1/T$; the blue lines highlight the range of thermally activated behaviour. c: Temperature dependence of the ideality factor $\eta$; the red line is a guide to the eyes.

d: Photoresponse of the current-voltage characteristics, shown by the arrows. For all measurements, a current of 50 mA was briefly applied to switch the sample into the “low resistance” state (purple triangle of Fig. 2b). For temperatures above $T^*$, the characteristics present an increase of voltage under illumination in the whole current range. Below $T^*$, the voltage is reduced upon illumination at small currents, but enhanced at larger currents, after the switching.
Extended Data 4: **Comparison of illumination with infrared light and with black-body radiation.** a: The measurements with the infrared source (LED) and under black-body radiation from room temperature give similar results (in red). Whereas with the full thermal shielding, the anomaly at $T^*$ is barely visible (black line), a small anomaly appears with incomplete thermal shielding (black points). In this case, the resistance below $T^*$ slowly drifts to lower values (orange points) as shown in panel b.
Extended Data 5: **Details on the illumination/relaxation process at 7 K.**

**a:** Normalized resistance during illumination and relaxation (black points). The red lines correspond to fits using stretched exponentials, with the constraint \( R_{t \to \infty} = R_0 \) for the relaxation process. During illumination, an initial fast exponential decay is observed (green line); we attribute it to overheating when the LED is switched on.

**b:** Relaxation process in linear scale with the fit. During relaxation, in 11 hours, the resistance has recovered less than 2% of its initial value.
Extended Data 6: **Tr-ARPES for several pump-probe delays at 7 K.**

a: Spectra around the $\Gamma$ point in the bulk-insulating sample ($x = 0.025$) without (left) and with (right) a pump, at the longest possible pump-probe delay of 4 $\mu$s, where a surface shift of 93 meV is still present. On top is a sketch of the pump-probe procedure. 

b: Same as a in the bulk-metallic sample ($x = 0.064$).

c: Tr-ARPES spectra at several pump-probe delays (in ps) in the bulk-insulating sample ($x = 0.025$). The negative delay is equivalent to a pump-probe delay slightly shorter than 4 $\mu$s.

d: Same as c in the bulk-metallic sample ($x = 0.064$).

e: Variation of the intensity as a function of the pump-probe delay in both samples, obtained by subtracting the intensity of the spectrum at 4 $\mu$s (average of 10 images) from the one of each spectrum at various pump-probe delays. The interval of the integration was over the angle [−14.5°, 14.5°] and the energy $E > 0$ (states above the Fermi level).