Time- and Momentum-resolved Signatures of Edge States in a 2D Topological Insulator

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Two-dimensional quantum spin Hall (QSH) insulators are a promising material class for spintronic applications based on dissipationless topologically-protected spin currents in their edges. Yet, they have not lived up to their technological potential, as experimental realizations are scarce and limited to cryogenic temperatures. These constraints have also severely restricted the characterization of their dynamical properties, imperative for the design of QSH devices operating under nonequilibrium conditions. Here, we report on the electron dynamics of the novel room-temperature QSH candidate bismuthene after photoexcitation using time- and angle-resolved photoemission spectroscopy. We map the transiently occupied conduction band and observe a metallic dispersive feature within the bulk band gap – a signature of topological edge states. Our analysis of hot photocarrier lifetimes provides insight into the microscopic scattering processes and the key role of edge states. The demonstration of the large bulk band gap and stability of edge states at room temperature marks a critical step towards QSH applications.

Two-dimensional quantum spin Hall (QSH) insulators are a promising platform for spintronic devices are two-dimensional (2D) topological insulators (TIs) [1]. Based on the quantum spin Hall (QSH) effect, 2D TIs feature an insulating band structure in their interior (here referred to as 2D bulk) surrounded by metallic states at their edges. These helical edge states (ESs) are characterized by spin-momentum locking, allowing for spin currents with opposite polarization for forward and backward-moving electrons. As they are topologically protected by time-reversal symmetry against single-particle backscattering, they also enable dissipationless transport [2, 3]. A modification of this behaviour arises when pairs of helical ESs are in direct vicinity to each other. Mutual hybridization of nearby ESs leads to a mixing of different helicities, thereby opening backscattering channels and partially lifting topological protection [4, 5]. Connected with their topological properties, ESs exhibit a distinctive electronic dispersion connecting the bulk valence and conduction bands [3]. Thus, any practical application based on helical ESs requires not only a large bulk band gap preventing the interference with thermally excited bulk carriers at room temperature, but also a thorough characterization of the energy-momentum distribution of bulk and edge states. Yet, so far band structure investigations of 2D TIs are scarce [6–8] and a demonstration of the elusive ESs using a momentum-resolved probe has proven challenging, as they constitute only a marginal fraction of the total surface area.

While angle-resolved photoemission spectroscopy (ARPES) has been pivotal for understanding the electronic structure of 3D TIs, the 3D analogues of QSH insulators [9–11], it is only sensitive to states populated at thermal equilibrium. However, depending on the Fermi level position, a clear separation of edge and bulk states can be difficult. In this light, time-resolved ARPES (trARPES) has proven itself vital by granting access to the energy- and momentum-dependent electron dynamics after femtosecond (fs) optical excitation, allowing to map the transiently populated topological states within the bulk band gap [12–15]. Furthermore, trARPES allows visualizing the motion of Dirac fermions in momentum space [16] and accessing microscopic
scattering processes, as demonstrated, e.g., in 3D TIs [17, 18]. In view of QSH devices operating under nonequilibrium conditions, it is critical to gain a similar understanding of the ultrafast dynamics of 2D TIs, in particular of the role of 1D ESs in scattering and energy redistribution processes.

A promising platform to address this knowledge gap is the room temperature QSH candidate bismuthene, i.e., a monolayer of bismuth atoms arranged in a planar honeycomb geometry on a silicon carbide SiC(0001) substrate [19]. Spatially resolved scanning tunneling spectroscopy (STS) measurements have demonstrated a large band gap of $\sim 0.8$ eV in bulk areas, far greater than in any other QSH system [6–8, 20–24], and conductive 1D states at exposed sample edges near substrate terrace steps [19, 25], as illustrated in Fig. 1a. Intriguingly, in topologically nontrivial materials, additional ESs can arise within the bulk areas at extended 1D defects [26, 27]. Recently, such ESs have been observed within the 2D bulk of bismuthene along structure-induced domain boundaries [28]. As pairs of helical ESs emerge at the zigzag edges on either side of these boundaries, as schematically depicted in Fig. 1a, their coupling lifts the topological protection, evidenced by trivial single-particle backscattering, which is absent in topologically-protected exposed ESs at sample edges [25]. Thus, bismuthene serves as a unique platform to investigate the dynamical properties of exposed and coupled ESs.

Fig. 1: Experimental scheme and sample topography. a, Illustration of the trARPES experiment. An optical pump pulse excites the bismuthene sample, followed by an XUV pulse that probes the electronic distribution after a time delay $\Delta t$. The green and blue arrows represent the two spin channels of the coupled ESs at a domain boundary and of the exposed ESs at a substrate step edge. b, STM constant-current image of bismuthene on a planar SiC substrate. A meandering network of domain boundary segments (bright ridges) intersects the bismuthene film into connected domains. Inset: Close-up of the Bi honeycomb lattice. c, STM image of bismuthene on a 4° miscut substrate featuring a high density of unidirectional SiC terrace steps. Inset: Bi honeycombs near a step edge. Scale bars b,c, 50 nm; insets 1 nm. d, Constant-energy contours with radius $k_\perp \sim 2 \AA^{-1}$ of bismuthene on a planar substrate after photoexcitation ($h\nu = 1.55$ eV, $\Delta t = -75 \ldots + 75$ fs). Two exemplary BZs and high-symmetry points are indicated.

Here, we investigate the ultrafast electron dynamics of photoexcited bismuthene at room temperature using trARPES, as illustrated in Fig. 1a, allowing us to access the microscopic scattering channels from the dynamics of the nonequilibrium state prepared by the optical excitation. Combining a hemispherical analyzer and a time-of-flight momentum microscope for photoelectron detection [29, 30], we map the transently populated conduction band structure and confirm the existence of a wide indirect bulk band gap of $\sim 0.82$ eV. In addition, we identify a faint metallic feature that connects bulk valence and conduction bands, which we attribute primarily to coupled ESs at domain boundaries – in general agreement with theoretical band structure predictions. Tracking the full relaxation pathway of hot photocarriers across the entire first Brillouin zone (BZ) yields additional evidence for the presence of metallic ESs, as these topological in-gap states enable a surprisingly efficient relaxation of excited carriers on a picosecond (ps) timescale.

**Bismuthene samples.** To investigate the role of coupled and exposed ESs, we compare the electron dynamics for two different types of samples, namely bismuthene epitaxially grown on (i) planar and (ii) highly miscut SiC(0001) substrates (see Methods). Bismuthene on a nominally planar substrate with its large terraces hosts mostly the coupled ESs at phase-slip domain boundaries [28], as displayed in the scanning tunneling microscopy (STM) image in Fig. 1b.
In contrast, intentionally miscut substrates allow adjusting the density and orientation of step edges and thus enable a controlled formation of exposed ESs. By preparing bismuthene on a 4” miscut SiC substrate, we achieve a high density of unidirectional exposed ESs along the parallel substrate step edges, see Fig. 1c. However, as domain boundaries within the terraces give rise to additional coupled ESs, bismuthene prepared on the miscut substrate hosts both coupled and exposed ESs, see the analysis of the sample morphologies in Supplementary Fig. S1. As we employ a ~100 μm-sized probe beam for photoemission, each measurement corresponds to a macroscopic surface area containing a large number of ESs. Note that the 2D bulk band structure of bismuthene does not depend on the substrate miscut.

Excited-state mapping. We begin by mapping the electronic band structure of bismuthene upon photoexcitation, as shown in Fig. 1d. Strong spin-orbit coupling in combination with covalent bonding of the Bi atoms with the substrate opens a large band gap in the Dirac-like crossing at the $\overline{K}$ points of the hexagonal BZ [31]. Excitation with near-infrared optical pulses lifts charge carriers across the bulk band gap and transiently populates conduction band states localized at $\overline{K}$ and, slightly more pronounced, at the $\Gamma$ points of the first and second BZs 1 eV above the valence-band maximum (VBM). Next, we focus on a momentum cut along the $\Gamma-K$ direction, which features the region of the direct optical interband transition near $\overline{K}$ and the conduction-band minimum (CBM) at $\Gamma$. Consistent with previous studies [19], the equilibrium band structure of bismuthene, presented in Fig. 2a, features sharp, spin-orbit split low-energy valence bands at $\overline{K}$. Upon optical excitation, a weak excited carrier population at $\overline{K}$ and a distinct dispersive band at the CBM at $\Gamma$ emerge, displayed in Figs. 2b-c. Concurrently, the valence bands at $\overline{K}$ are depleted by the optical transition (blue coloured region in Fig. 2c), and their band width broadens due to scattering of the photoholes with excited quasiparticles [32, 33].

Band-gap renormalization by photo-doping is particularly pronounced in 2D materials due to reduced charge carrier screening [34]. To minimize this effect, we extract the direct and indirect band gaps using a low incident fluence of 0.14 mJ cm$^{-2}$, as shown in Figs. 2d-e. At $\overline{K}$, we find...
a direct band gap of 1.05±0.02 eV, extracted from the peak positions of Gaussian fits to the upper spin-orbit split band at the VBM and to the lowest-lying CB, which is in excellent agreement with density functional theory (DFT) calculations (1.07 eV [19]). The indirect band gap between the VBM at $K$ and the CBM at $\Gamma$, extracted using a Gaussian fit with an exponentially decaying background, amounts to 0.82±0.02 eV, which is in reasonable correspondence with the DFT value of 0.67 eV [19]. Furthermore, the experimental value also perfectly agrees with the momentum-integrated bulk band gap of $\sim 0.8$ eV obtained from STS measurements [19]. Additional measurements using 3.1 eV optical excitation, giving access to the full dispersion of the lowest-energy conduction band, are shown in Supplementary Fig. S3.

**In-gap states.** Intriguingly, in addition to the prominent bulk bands, we observe a faint intensity at $\Gamma$, reaching up to $E_{\text{VBM}}$ in equilibrium, as shown in Fig. 3a. Optical excitation reveals the cone-shaped dispersion of this unusual in-gap state, which extends into the CBM (Fig. 3b), resulting in the absence of an explicit gap between conduction and valence bands (black arrow in Fig. 2e). Such an hourglass-shaped dispersion is a hallmark of topological ESs, and in general agreement with theoretical predictions for exposed ESs, see Fig. 3c. However, from exposed ESs at the unidirectional substrate steps, we would expect a clear 1D signature in momentum space, i.e., a dispersionless band structure along the quantum confined direction. In contrast, we find the in-gap feature to be approximately isotropic within the 2D plane, i.e., azimuthally symmetric (see Supplementary Fig. S4). Furthermore, since we observe similar spectral features for both sample types (see Supplementary Fig. S5), while exposed ESs at substrate steps have a much higher density on the miscut sample, this class of ESs alone cannot explain our observations. Rather, we attribute the in-gap feature to coupled pairs of ESs that arise in direct proximity to each other along phase-slip domain boundaries, as illustrated in Fig. 3d. These boundaries are present in both sample types and result from the fact that the $(\sqrt{3} \times \sqrt{3})$ Bi honeycombs can have three distinct registries with respect to the substrate lattice, causing the growth of domains. The resulting zigzag domain boundary sections switch their azimuthal orientations between all possible $\Gamma$-$M$ directions of the BZ, as shown in Fig. 1b. Depending on the orientation of individual boundary segments with respect to the measurement plane, the respective coupled ES dispersion gets smeared out azimuthally. As each trARPES measurement corresponds to the spectral superposition of a multitude of 1D ESs with various orientations, the coupled ESs appear as a rotationally symmetric dispersive feature that is most pronounced at $\Gamma$ where individual states overlap, accompanied by a weak intensity background across the entire BZ. Also the faint intensity of the in-gap states on the order of a few per cent of the bismuthene bulk bands at $K$ is consistent with the assignment to ESs, as the domain boundaries constitute only a fraction of the probed surface. The pronounced dispersion of the in-gap feature further allows us to exclude impurities as the origin of the metallic states, as such states lack a clear momentum dependence [35].
Fig. 4: Carrier relaxation dynamics. a, Excited-state band dispersion after 1.55 eV optical excitation ($F=0.50$ mJ cm$^{-2}$, miscut substrate). b, Normalized photoemission intensities corresponding to boxes 1 to 3 indicated in panel a as a function of pump-probe delay. The solid lines show best fits using a single-exponential decay convolved with a Gaussian (Gaussian width as free parameter). The fit parameters $t_{\text{max}}$ (temporal intensity maximum) and $\tau$ ($1/e$ decay constant) are given with one standard deviation as uncertainty. Inset: dynamics near $\Delta t = 0$ fs. The grey dashed line indicates the temporal profile of the pump-laser pulse. c, Temporal maximum $t_{\text{max}}$ and d, carrier lifetimes $\tau$ from bin-wise energy- and momentum-dependent decay fits. For this, the transient photoemission intensities are extracted across the energy-momentum region shown in panel a using a sliding-window integration ($\Delta E = 0.2$ eV, $\Delta k_x = 0.2$ Å$^{-1}$) and fitted using the function described above. Regions with large fit uncertainties ($\sigma_{t_{\text{max}}} > 4$ fs, $\sigma_\tau > 30$ fs) are masked in grey. e, Schematic scattering processes within the DFT band structure (see text). The in-gap states are indicated in blue.

Carrier relaxation dynamics. Next, to elucidate the possible role of the topological ESs as quasiparticle scattering channels in the photocarrier relaxation processes of bismuthene, we investigate the excited-state population dynamics after 1.55 eV optical excitation, focusing on the $\Gamma$-$K$ direction (Fig. 4a). As the transient photoemission intensities in Fig. 4b show, a CB population builds up first near $K$ (box 1 in Fig. 4a), reaching its maximum intensity at 27 fs. The apparent delay with respect to temporal pump-probe overlap is due to a build-up of the excited-state population in energy-momentum space (Fig. 4c) and provide a concise overview of the lifetimes associated with particular states (Fig. 4d).

Combining the results of both maps yields a detailed picture of the complete carrier relaxation pathway, schematically depicted in Fig. 4c: (1) Carriers are initially injected by a vertical interband transition into the CB near $K$ using 1.55 eV radiation. While the faint states at $E_{\text{VBM}}$ near $\Gamma$ could lead to additional vertical transitions, their density is several orders of magnitude below the bulk bands, and no detectable initial excited-state population is observed at $\Gamma$. (2) The hot electrons redistribute by intervalley scattering, which spreads the carriers over an extended momentum region into the $\Gamma$ valley on a 10 fs timescale, a phenomenon commonly observed in photoexcited semiconductors [36–39]. (3) Subsequently, hot carriers relax towards the CBM at $\Gamma$ via electron-electron and electron-phonon scattering within ~50 fs. Although bulk bismuthene exhibits an indirect band gap of several 100 meV, the lifetime of the conduction band popula-
tion is only on the order of few 100 fs – orders of magnitude lower than in conventional indirect semiconductors [36, 40–42]. These ultrashort lifetimes are further evidence for the presence of a continuous density of ESs within the band gap at $\Gamma$, as (4) the conductive in-gap states facilitate a highly efficient carrier relaxation, mediated by electron-electron and electron-phonon scattering. Finally, within $\sim 1.5$ ps, the in-gap states above the VBM are fully depleted. Equivalent relaxation processes are found in bismuthene on a planar substrate, see Supplementary Fig. S6.

The itinerant ESs enable a rapid depletion of the conduction band population, which requires transport of excited charge carriers from bulk regions to metallic states at domain boundaries and substrate step edges. As the average spatial distance to a border that hosts metallic ESs is only on the order of few nanometers, see Supplementary Fig. S1, decay times on the fs timescale are in general agreement with diffusive transport of photocarriers on the surface [43]. In agreement with these considerations, we find an increase of the population lifetime on the planar substrate by $\sim 30\%$ (Supplementary Fig. S6), as the average spatial distance and thus the resulting diffusion time to a border is slightly larger than for the miscut sample.

**Hybridization effects.** The hybridization of coupled ESs may also speed up the relaxation of the excited ES population. The lifted topological protection due to the mixing of different helicities enables elastic single-particle momentum- and spin backscattering, which extends the phase-space for inelastic scattering events, such as electron-hole creation and interband scattering. In 3D TIs, it has been shown that the breaking of time-reversal symmetry by magnetic impurity doping significantly lowers the lifetime of the topological surface state population due to the availability of additional scattering channels [18, 44]. As the domain walls in bismuthene feature a plenitude of irregularities and kinks, emerging defect-induced states in combination with the lifted topological protection might explain the observed short population lifetimes in bismuthene. In addition, the hybridization of nearby pairs of helical ESs is expected to open up a small energy gap at the crossing of the ESs [4, 26], see the schematic dispersion in Fig. 3d. However, due to our limited experimental energy resolution of $\sim 150$ meV and due to local variations of the chemical potential on the order of $\sim 100$ meV, as observed in STS measurements, we do not resolve a gap opening at $\Gamma$.

A clear assignment of the influence of the exposed ESs appears difficult. The continuous in-gap spectral weight is approximately azimuthally symmetric and present in both sample types and was thus assigned to coupled ESs at domain boundaries. Yet, the miscut sample exhibits increased in-gap spectral weight, a more pronounced ES dispersion, as shown in Supplementary Fig. S5, and shorter population lifetimes at the CBM, suggesting an additional contribution of exposed ESs. Here, future developments in (time-resolved) nano-ARPES featuring a nanometer spatial resolution may allow isolating the spectral features of exposed ESs at substrate terrace steps. Additionally, optimizing sample growth conditions may allow decreasing the density of domain boundaries, facilitating a further separation of exposed and coupled ESs.

**Conclusions**

In summary, we experimentally map out the electronic band structure of the quantum spin Hall insulator bismuthene after near-infrared photoexcitation. In addition to its wide indirect bulk band gap of $\sim 0.8$ eV, we identify the metallic dispersive spectral fingerprints of edge states that arise at domain boundaries and step edges of the bismuthene sample. We show that these edge states persist at room temperature and under strong optical excitation, which, in combination with the large fundamental bulk band gap, may facilitate quantum spin Hall applications under ambient conditions. Furthermore, analysis of the microscopic scattering pathway of hot photocarriers reveals exceptionally fast carrier relaxation dynamics governed by the metallic edge channels. Our results provide important information relevant to the transport properties in these topological states. Yet, the formation of edge states with lifted topological protection along extended 1D defects may pose challenges for applications utilizing the spin-selective transport along exposed sample edges [27, 45]. Nevertheless, while finite-size effects may lift the topological protection of edge states emerging at domain boundaries [28], their occurrence further substantiates the nontrivial topology of bismuthene.
Methods

Sample preparation and STM measurements.

Bismuthene was epitaxially grown on n-doped 4H-SiC(0001) substrates (0.01 - 0.03 Ω·cm, carrier concentration $\sim 10^{18} - 10^{19}$ cm$^{-3}$, planar and 4° miscut) in ultra-high vacuum < $10^{-10}$ mbar. Prior to growth, a smooth H-terminated SiC surface was prepared by hydrogen-based dry-etching. Growth was performed at $\sim 600^\circ$C to thermally desorb the surface H-termination, while simultaneously offering Bi atoms from a commercial effusion cell [19]. Successful growth of low-defect bismuthene samples was verified using low-energy electron diffraction and scanning tunneling microscopy. The overview topography maps (Fig. 1b-c) were recorded at $T = 4.35$ K, setpoint voltage $U = 3.0$ V and current $I = 50$ pA (insets: $U = -0.8$ V and $I = 100$ pA).

Time-resolved ARPES measurements.

After characterization, the samples were transferred to the trARPES setup using a UHV suitcase at $p < 10^{-10}$ mbar. All measurements were performed at room temperature using a laser-based high-harmonic-generation trARPES setup (p-polarized probe at $h\nu_{\text{probe}}=21.7$ eV, s-polarized pump at $h\nu_{\text{pump}}=1.55 / 3.10$ eV, 500 kHz repetition rate, $\Delta E \sim 150$ meV, $\Delta t \sim 40$ fs) with a 6-axis manipulator (SPECs Carving) [29]. Photoelectrons were detected either with a hemispherical analyzer (SPECs Phoibos 150) or a time-of-flight momentum microscope (SPECs METIS 1000) [30]. The momentum microscope allows for a parallel acquisition of the 3D photoelectron distribution $I(E_{\text{kin}}, k_x, k_y)$ across a large energy and momentum range, and was thus utilized for overview measurements of the electronic band structure (see Fig. 1d). In contrast, the hemispherical analyzer allows for fast data acquisition within a limited energy-momentum window, and was thus used to map selected high-symmetry directions (see Fig. 2 and Fig. 3a,b). The momentum-microscopy measurements were performed at an extractor-sample distance of 4 mm and an extractor voltage of 6 kV. The XUV probe spot size (FWHM) was $\sim 80 \times 80$ µm$^2$. The pump spot sizes were $\sim 260 \times 200$ µm$^2$ ($h\nu=1.55$ eV) and $\sim 510 \times 475$ µm$^2$ ($h\nu=3.10$ eV). All fluences stated in the text correspond to incident fluences. Temporal pump-probe overlap was determined from the pump-laser-induced depletion of the valence band population, as shown in Supplementary Fig. S8.

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Author contributions

J.M., M.D., R.S., S.D., S.B., T.P., A.N. and L.R. carried out the trARPES experiments; J.M. analyzed the trARPES data; R.S. prepared and characterized the samples and analyzed the STM data; G.L. performed the DFT calculations; J.M. wrote the manuscript with support from L.R., R.S., R.E. and R.C.; L.R., R.E., M.W. and R.C. provided the experimental infrastructure; all authors commented on the paper.

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Supplementary Information for "Time- and Momentum-resolved Signatures of Edge States in a 2D Topological Insulator"

Supplementary Figures

Supplementary Fig. S1: Sample morphology. a, b, STM constant current images of bismuthene on a planar and a miscut substrate, respectively. The miscut SiC substrate in b, is characterized by unidirectional substrate steps every ~15 nm that induce exposed bismuthene edges. While both the morphology of the planar and the miscut bismuthene samples feature domain boundaries, the miscut bismuthene sample exhibits a significantly larger exposed edge density (> factor 5). Scan parameters: a, $V_{set} = 3.0 \text{ V}, I_{set} = 50 \text{ pA}, T = 4.35 \text{ K}$; b, $V_{set} = 2.6 \text{ V}, I_{set} = 30 \text{ pA}, T = 4.35 \text{ K}$. c, d, Binary masks marking domain boundaries and defective areas on the planar and miscut samples from a and b, respectively. e, f, Heat-maps indicating the spatial distance to a boundary calculated from the binary masks in c and d, respectively. g, h, Distribution and cumulative distribution, respectively, of the spatial distances of the planar and miscut samples extracted from e and f, respectively. The average spatial distance to a border for a planar sample is ~2 times larger than for a miscut sample.
Supplementary Fig. S2: Electronic band structure maps of bismuthene on a planar substrate. a, False colour plots of the trARPES measurements along the Γ-K direction in equilibrium and b, after optical excitation ($h\nu = 1.55$ eV, incident fluence $F=0.50$ mJ cm$^{-2}$).

Supplementary Fig. S3: Conduction band dispersion after photoexcitation. Photoemission intensity along the high-symmetry momentum directions after 3.1 eV optical excitation ($F=0.03$ mJ cm$^{-2}$) at temporal pump-probe overlap. DFT calculations are shown in black.
Supplementary Fig. S4: Equilibrium constant-energy contour of bismuthene. (radius $k_{\parallel} \sim 2 \text{Å}^{-1}$, miscut substrate). The first BZ and high-symmetry points are indicated. The white circles mark the $\Gamma$ points of the second BZs featuring faint spectral weight at the VBM corresponding to the in-gap feature discussed in the main text. Since these features are approximately rotationally symmetric, we rule out a dominant contribution from unidirectional exposed ESs at substrate terrace steps, as these are expected to feature a unidirectional 1D signature in momentum space. Due to a reduced sensitivity of the central region of the detector, the intensity of the faint in-gap feature at the $\Gamma$ point of the first BZ is below the detection limit. To correct for momentum distortions arising from electric field inhomogeneities of the extractor field due to the geometry of the sample mount, we applied a distortion correction as described by Xian et al. [1] Note that, near the edge of the photoemission horizon, certain momentum distortions are not captured by the correction.

Supplementary Fig. S5: Metallic feature at $\Gamma$. a, Equilibrium band dispersion of bismuthene on a miscut substrate. A faint dispersive feature near the VBM is identified, which we assign to topological ESs. In order to capture the 1D dispersion of the exposed ESs, the unidirectional substrate step edges are oriented parallel to the entrance slit of the hemispherical analyzer. b, Band dispersion of bismuthene on a planar substrate, exhibiting a similar, slightly less pronounced feature at $\Gamma$. c, Corresponding EDCs at $\Gamma$. Both samples show a faint but distinct intensity up to $E_{\text{VBM}}$, which is roughly a factor 2 more intense for the miscut substrate.
Supplementary Fig. S6: Photocarrier lifetimes. a, Normalized photoemission intensities of the conduction band populations at $K$ and $\Gamma$ for bismuthene on miscut and planar substrates ($F=0.50 \text{ mJ cm}^{-2}$) versus pump-probe delay. The inset indicates the energy-momentum regions of interest within the DFT band structure of the respective time traces (equivalent to boxes 1 and 2 in Fig. 4a). Single-exponential decay fits reveal similar $1/e$ lifetimes of the populations at $K$ for both substrate types, and slightly increased lifetimes at $\Gamma$ for the planar substrate. b, Extracted lifetimes for both substrate types as function of incident fluence. The dashed lines serve as guides to the eye. While the overall lifetime increases with fluence, the lifetime at $\Gamma$ for the planar substrate is systematically higher with respect to the miscut substrate for all applied fluences. The error bars correspond to one standard deviation of the fit parameter $\tau$.

Supplementary Fig. S7: Electron diffraction of the discussed bismuthene samples. a, Low-energy electron diffraction of bismuthene on a miscut SiC substrate recorded at an energy of 50 eV and b, on a planar SiC substrate recorded at an energy of 48 eV. Sharp, intense diffraction spots and a weak diffuse background signal indicate high-quality sample surfaces. The yellow arrows in a mark stripe-like elongations of the SiC spots corresponding to unidirectional substrate step edges. Exemplary SiC 1x1 and Bi $\sqrt{3}x\sqrt{3}$ R30° reciprocal unit cells are indicated.
Determination of temporal pump-probe overlap

To determine the temporal pump-probe overlap $\Delta t = 0 \text{ fs}$, we extract the initial depletion of the valence band population at $\mathbf{K}$ (red box in Supplementary Fig. S8a) resulting from the vertical optical transition. The extracted photoemission intensity as function of pump-probe delay is fitted using an error-function, see Supplementary Fig. S8b. Here, the central position of the error function corresponds to the temporal peak of the optical pump pulse, $t_0$. For all measurements presented in this manuscript, we calibrate the pump-probe delay such that $\Delta t = 0 \text{ fs}$ corresponds to $t_0$.

![Supplementary Fig. S8: Arrival time of the optical excitation pulse. a, Equilibrium ARPES measurement of the $\Gamma$-$\mathbf{K}$ direction. b, Normalized photoemission intensity extracted from the red box in panel a as function of pump-probe delay (red circles, $h\nu_{\text{pump}} = 1.55 \text{ eV}$, incident fluence $F=0.50 \text{ mJ cm}^{-2}$). The black solid line marks the best fit using an error function. Fit coefficient values of the temporal peak $t_0$ and full width at half maximum of the pump pulse are stated in the figure, respectively. One standard deviation is given as uncertainty.](image)

Finite-size effects in coupled edge states

As evidenced by STS, mutual hybridization lifts the topological protection of coupled ESs at domain boundaries [2]. This gives rise to a partial reflection of quasiparticles at local perturbations of the domain boundary, such as kinks or defects, which leads to intriguing standing-wave patterns of the local density of states within individual domain boundary segments. As a result, depending on the length of a particular segment, the associated coupled ES spectrum features specific discrete states superimposed on a continuous metallic background. In trARPES, however, such a quantized structure is not observed. Since each measurement corresponds to a large number of domain boundary segments, and as their length and thus the discrete energy states are statistically distributed, macroscopic averaging leads to the observed continuous in-gap spectrum. In addition, due to the fragmentation of the ESs into nanometer-sized segments, a deviation from the theoretical dispersion of infinitely extended coupled ESs (see Fig. 3d) is expected. Nevertheless, the experimentally observed cone-shaped dispersion is in general agreement with band structure calculations of infinitely extended coupled ESs.

Supplementary References

1. Xian, R. P., Rettig, L. & Ernstorfer, R. Symmetry-guided nonrigid registration: The case for distortion correction in multidimensional photoemission spectroscopy. *Ultramicroscopy* **202**, 133–139 (2019).
2. Stähler, R. *et al.* Lifting topological protection in a quantum spin Hall insulator. *Unpublished manuscript* (2021).