Ultrafast Band-edge Optical Anisotropy and Carrier Dynamics in Te Nanosheets

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Abstract

Trigonal tellurium (Te) is an anisotropic chiral semiconductor that holds great promise as the foundation for next generation optoelectronic and thermoelectric devices. Engineering these devices, however, relies critically on details of the band-edge optical response and carrier decay dynamics, which are poorly understood in Te. Here we employ polarized transient mid-IR reflectance spectroscopy to investigate both its complex electronic structure as well as carrier dynamics within the extended bulk band structure. The transient spectra reveal a series of optical transitions around the H- and L-points of the Brillouin zone and the transition energies are found to be very sensitive to the laser polarizations perpendicular (E ⊥ c) and parallel (E ∥ c) to the c-axis of the Te crystal. Optical transitions are clearly seen between uppermost H4, H5 and H6 valence bands (VB) and the lowest lying H6 conduction band (CB). The fundamental gap (H4 → H6) is observed at 0.32 eV with both polarizations, while the higher lying transition (H5 → H6) is only observed for E ∥ c. The energies of both transitions measured with E ∥ c are strongly modulated as photoexcited carriers relax to ground state, suggesting transient band modifications by photoinduced strain in the nanosheet. This suggests a transient lifting of the spin degeneracy at the H6 CB minimum, a proposed Weyl node. The majority of photoexcited carriers near the band edge are seen to decay within 30 ps while higher lying transitions observed near 1.2 eV appear to have substantially longer lifetimes, potentially due to contributions of intervalley processes in the recombination rate. These new findings shed light on strong correlation between photoinduced carriers and electronic structure in anisotropic crystals and provide a new pathway for designing Te-based novel devices.
Introduction

The landmark isolation of single layer graphene from graphite has stimulated extensive research interest in a number of van-der Waals (vdWs) materials due to the potential of revealing new physics at nanoscale and offering new building blocks for high performance electronic devices. Beyond graphene and widely known semiconducting transition metal dichalcogenides (TMDs), a variety of exotic vdWs materials such as topological insulators (TIs) and Weyl semimetals (WSMs) have been recently discovered, which display unique electronic structure and chiral spin texture on the Fermi surface. Most of these exotic materials are compound materials involving heavy elements such as Bi, Sb, Te, Se, etc. and, therefore, the strong spin-orbit interaction (SOI) is the key for modifying the basic electronic structure. The group-V elemental tellurium (Te) has gained renewed interest in this category due to recent predictions and findings of unique spin texture and topological features in the band structure. Recent progress in isolating two-dimensional (2D) Te nanostructures and fabrication of high mobility field-effect devices has increased its potential use for both optoelectronic and thermoelectric devices.

Unlike the widely known planar 2D vdWs materials, trigonal Te is a 1D vdWs crystal consisting of 3-fold helices of Te atoms, which are weakly coupled in a hexagonal close-packed array. Strong covalent bonds form between nearest-neighbor atoms in each helix, which spirals around an axis parallel to the c-axis (see Fig. 1a) and so perfect single crystals can display either right-handed (space group: $P3_121$) or left-handed (space group: $P3_221$) helical screws. Such handedness ensures the lack of mirror symmetry in this non-centrosymmetric crystal and so trigonal Te is an example of a chiral material. A number of gyrotropic properties have been observed in Te due to structural chirality such as a strong optical rotatory power, circular photogalvanic effect, current-induced magnetization, etc. This makes trigonal Te a unique material for potential applications in polarization optics, multiferroics, and spintronics. The naturally occurring lack of mirror symmetry and the breaking of the space-inversion symmetry in the crystal structure result in a unique radial spin texture in the band structure of Te, in contrast to typical Rashba systems or topological materials. The spin degeneracy of the uppermost valence bands (VBs) near the band gap, i.e., at the H- or H’-points in the Brillouin zone, is lifted in momentum space due to SOI and the breaking of inversion symmetry while the lowest conduction band (CB) at the gap is doubly spin-degenerate and the degeneracy is protected by the three-fold screw symmetry of the helices. Such a stable insulating phase holds in trigonal Te under ambient pressure but transforms to a metallic phase under hydrostatic pressure that closes the band gap through structural phase transitions. Recently, the band structure of Te was investigated including consideration of SOI and the topological nature of the electronic structure was identified with the existence of Weyl nodes at and
near the spin degenerate points around the H-point, particularly the $H_6$ CB minimum.\textsuperscript{10, 11} The topological phase transition from a trivial semiconductor to a Weyl semimetal (WSM) phase is predicted under applied external pressure when the spin-polarized uppermost VB and CB are inverted across the band gap.\textsuperscript{9, 30} Since a strong piezoelectric effect has been reported in bulk Te and nanostructures,\textsuperscript{31-33} strain can also be generated in response to an applied electric field and vice versa. Therefore, it is interesting to explore electronic structure under laser excitation that can eventually provide a non-destructive pathway to manipulate and control topological phases in Te. The unique electronic structure in this chiral material offers the potential to exploit both the electronic charge and spin degrees of freedom, even without magnetism for potential applications in spintronics.

Despite renewed interest provided by new insights through calculations of electronic structure, there are very few experimental investigations of polarization resolved optical transitions and photoexcited carrier lifetimes and scattering dynamics in trigonal Te particularly near the band-edge region. Most previous optical studies have focused on investigating ground-state optical absorption properties depending on light polarization with respect to crystal orientation, \textit{i.e.}, either parallel or perpendicular to the c-axis.\textsuperscript{18, 34-40} The main finding of ground-state band-edge absorption anisotropy in these publications is heavily discussed and its origin is explained on the basis of the symmetry properties of the Te crystal.\textsuperscript{39, 41} However, outside the band-edge region, the Te band structure displays a large number of band degeneracies and a multi-valley nested structure that supports high thermoelectric efficiency in Te-based thermoelectric devices.\textsuperscript{42} Therefore, it is of fundamental interest to investigate such anisotropic response in technologically relevant Te nanosheets from the band edge to higher lying states in both the conduction and valence bands. Probing carrier dynamics around such a wide energy region provides a unique opportunity to investigate inter- and intra-valley carrier decay processes in addition to the fundamental recombination lifetime.\textsuperscript{43} Such information is a critical issue in the development of Te-based thermoelectric, electronic and optoelectronic devices.

In this work, we use femtosecond mid-infrared pump-probe transient reflectivity measurements to investigate the optical transitions and energy relaxation of photoexcited carriers immediately after photoexcitation. Hydrothermally synthesized Te nanosheets (tens of microns across and thicknesses of 20 – 30 nm) are dispersed on a silicon substrate with the c-axis lying parallel to the surface. The substrates are mounted onto the cold finger of a microscope cryostat and studied using transient reflectance (TR) spectroscopy at 10 K. (TR spectroscopy at 300 K is presented in the Supplementary Information) The transient response of the sample excited with a 1.51 eV pump pulse is probed with a mid-infrared probe pulse polarized parallel and perpendicular to the c-axis of the Te crystal. The probe energy is tuned over a
wide spectral range (0.3–1.2 eV), which covers the fundamental band-edge near the H-point as well as higher bands at both the H- and L-points of the Te bulk Brillouin zone. Measured polarized TR spectra at different delay times are analyzed with the support of modeling, and transition energies are compared with band-structure calculations. The basic band parameters such as the band-gap and Fermi energy (i.e., carrier density) are estimated by model fitting of the lowest energy transient spectra. Energy and polarization dependent kinetics of the transient response is evaluated to determine the dominant relaxation channels of photoexcited carriers in the Te band structure. Finally, the implications of these results on potential applications are discussed.

Results

Sample characteristics. Tellurium (Te) crystallizes into covalently bonded helical chain of atoms held together by weak van der Waals forces in a hexagonal array.\(^\text{16}\) The Te chains are parallel to the c-axis of the hexagonal crystal while the basal plane or \(ab\) – plane is perpendicular to the chain, as indicated in Fig. 1a. The Tellurium nanostructures studied here are chemically synthesized using a hydrothermal process and dispersed onto a Si substrate with a 300 nm SiO\(_2\) capping layer.\(^\text{15}\) Due to the nanowire-like growth mechanism, the c-axis of these nanostructures are lying in the plane, which is markedly different than in typical epitaxially grown thin films where the c-axis is along the growth direction and perpendicular to the surface. The anisotropy of the weakly bonded chain structures can easily be studied in this geometry. Details of growth and transfer of Te samples are described in the Methods section. Fig. 1b shows large area tapping mode AFM height images of the nanostructures and their orientation with respect to the c-axis of the hexagonal lattice. The thickness of these nanostructures varies between 20 nm to 30 nm, which are estimated by AFM height profiles across the nanosheets, as shown on the bottom left of Fig. 1b. The surface morphology, as shown in enlarged scans on the right, displays an atomically smooth surface, without any noticeable degradation of the surface.

The orientation of the samples was confirmed using polarized micro-Raman spectroscopy measurements using a 632.8 nm continuous wave laser source (see Fig. 1c). The laser polarization is set either parallel (\(E \parallel c\)) or perpendicular (\(E \perp c\)) to the c-axis. With \(E \parallel c\), we observe three well-resolved sharp Raman peaks at 119 cm\(^{-1}\), 90 cm\(^{-1}\) and 138.5 cm\(^{-1}\) corresponding to \(A_1\) (symmetric intra-chain breathing in the basal plane) and the doubly degenerate \(E(1)\) (rigid chain rotation in the basal plane) and \(E(2)\) (asymmetric stretching along the chain or the c-axis) modes, respectively, as indicated in Fig. 1c.\(^\text{44}\) The weak and broad peak at 266 ± 1 cm\(^{-1}\) corresponds to the second order harmonic of the \(E\)-mode. Both the \(E(1)\) and \(E(2)\) modes are infrared active while the \(E(1)\) mode is found to be sensitive to the laser
polarization with respect to the c-axis (see inset of Fig. 1c), which is consistent with previous studies.\textsuperscript{44} Logarithmic plots of the data confirm that the E(1) mode is symmetry forbidden for $E \parallel c$. 
Fig. 1. Structure and morphology of Te nanosheets. a. Crystal structure of trigonal Te (left image) in which spheres of different colors represent Te atoms within the helical chains (shaded region) arranged in a hexagonal array along the growth direction, i.e., c-axis. Pattern with blue lines shows a hexagonal unit cell along [001]. Right image is the top (surface) view of the crystal from [001] direction, showing ab-plane (basal plane) and surface lattice parameter (a₀). b. AFM topographies of the Te nanosheets used for optical measurements (symbolized by Te-1 and Te-2) and their cross section profiles (red and blue lines). Close-up height scan on Te-1 (dotted rectangle) is shown on bottom right, which exhibits relatively smooth surface with an average corrugation estimated to be < 2 nm. c. Representative Raman spectra acquired on these samples using an excitation source of 633 nm laser at two perpendicularly polarized configurations with respect to the c-axis, i.e., E ∥ c and E ⊥ c. Mainly three prominent optical modes, as indicated by A₁, E(1), and E(2) modes, respectively, are detected with E ⊥ c while only A₁ and E(2) modes are clearly visible with E ∥ c. Inset shows a log scale plotting of the data, showing that the E(1) mode is symmetry forbidden for E ∥ c. The Weak signal of second order harmonic of E-mode is also indicated by the symbol E'.

Polarized transient reflectance spectroscopy (TRS). The TR measurements on Te nanosheets is illustrated schematically in Fig. 2a. The Si/SiO₂ substrate with the Te nanosheet is mounted to the 10 K cold finger of a microscope-cryostat. A short 1.51 eV pump pulse (200 fs) is superimposed collinearly with a (200 fs) probe pulse of variable photon energies (0.3 to 1.2 eV) and focused onto a single Te nanosheet using a 40 × 0.5 NA reflective objective. The electric field polarization of the incident probe beam is oriented using a CaF₂ double Fresnel Rhomb rotator to be either parallel (E ∥ c) or perpendicular (E ⊥ c) to the c-axis of the Te crystal. The pump-induced change in the sample properties is measured by the change in the reflectivity of the probe beam with the pump pulse present, ∆R(E, t) = (Rₚₒₚᵣₑᵢₚₜₒᵣₚᵢₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋ₒᵣₑᵢₚₜ₋₀, R₀) as a function of both probe energy (E) and delay (t) of the probe pulse with respect to the pump pulse. The ∆R(E, t) data are normalized by the probe reflectance R₀ with the pump off at all probe energies E, and recorded as ∆R/R₀. Fig. 2b displays a false color map of the TRS spectra, ∆R/R₀ measured over a wide spectral region (0.3 – 1.2 eV) for the probe polarized parallel and perpendicular to the c-axis. Overall, the spectra show strong derivative-like anti-symmetric features in both the low-energy (∼0.3 – 0.5 eV) and high-energy (∼1.2 eV) regions and a relatively weaker and broader signal at around ∼0.7 eV, corresponding to a series of interband optical transitions. There are several noticeable short-lived and long-lived spectral features, which are sensitive to the polarization of the probe beam. The most interesting and noticeable polarization-dependent feature is clearly visible near the band edge (∼0.35 eV). With E ∥ c, a nearly overlapped additional anti-symmetric feature is observed at ∼ 0.45, which is not present for E ⊥ c, suggesting the first evidence of polarization-sensitive transient optical response in Te
samples. We first quantify each of these features and compare their energies with the ground-state band-to-band optical transitions as expected from band-structure calculations.

**Fig. 2.** Transient reflectance response of Te nanosheets near the bulk band-edge. a Schematic illustration of the polarization-resolved transient reflectance spectroscopy (TR) setup. The probe beam is polarized either parallel $E \parallel c$ or perpendicular $E \perp c$ to the c-axis of Te crystal through rotation of the polarization angle $\phi = 0^\circ$ or $\phi = 90^\circ$ relative to the c-axis. b Two-dimensional false color map of the pump-probe delay dependent polarized TR spectra over extended probe energies. A narrow region of probe energies between $0.72 – 0.8$ eV is missing due to technical limitations of the laser. Overall, strong features with distinctive dynamics at different energies are clearly visible. c TR spectra (blue spheres) acquired at 100 ps time delay with two orthogonal probe polarizations. Each spectrum is fitted with a simple model described in the main text (red dashed lines). Calculated moduli $\Delta \rho_j$ of each fit are also plotted with vertical offset (black lines). Both the model fits and the moduli show transient features corresponding to
the series of optical transitions in the Te bulk band structure. d Schematic band structure of bulk Te and possible optical transitions around the high symmetry H and L points of the Brillouin zone near the band-edge region. Observed transition energies in the TR spectra at different band-edge regions are indicated. On the right top, the first Brillouin zone of Te and various high symmetry points are indicated.

**Band-edge optical transitions:** We note that the main TR signal (see Fig. 2b) decays within first 30 ps while the residual signal persists over a long delay without substantial change in the spectral shape. Therefore, spectral slices at 100 ps delay (see Fig. 2c) are chosen from each polarization and both are normalized by the positive peak intensity for better visibility of weak spectral features. The derivative-like spectral features of the transient signal at low energies \((0.34 – 0.45 \text{ eV})\) exhibits difference for the two polarizations while the features around the high-energy region \((0.9 – 1.2 \text{ eV})\) are nearly identical. Each of these features corresponds to a change in the dielectric response near interband optical transitions. In order to determine the energies of optical transitions accurately, each \(\Delta R/R_0\) spectrum is analyzed by using a derivative Lorentzian line-shape functional form appropriate for excitonic transitions,\(^45\)

\[
\frac{\Delta R}{R_0}(E) \approx \sum_{j=1}^{n} \text{Re} \left[ A_j e^{i\varphi_j} (E - E_j + i\Gamma_j)^{-2} \right],
\]

where \(n\) represents the number of spectral functions for the possible interband transitions involved, \(E\) is the photon energy of the probe beam, and \(A_j, \varphi_j, E_j,\) and \(\Gamma_j\) are the amplitude, phase, transition energy, and the energy broadening parameter of the \(j^{th}\) feature, respectively. The least square fitting of measured spectra to Eq. (1), are shown with dashed-lines in Fig. 2c. The spectra with \(E \perp c\) can be fitted by three resonances \((n = 3)\) while the spectra with \(E \parallel c\) can be fitted by four resonances \((n = 4)\). Moduli of the individual resonances (showing approximate absorption profiles), which have been obtained from Eq. (1), are also overlapped with minor vertical shifts for clarity. The values of the transition energies obtained from line shape fitting are indicated by vertical dotted lines. The probable assignment of these transitions to particular features in the tellurium band structure is now discussed.

The band extrema for the valence and the conduction bands are located near the high symmetry points H and H’ at the corners of the hexagonal Brillouin zone in Te (see inset to Fig. 2d). We compare the transition energies from transient reflectivity measurements with the detailed band structure around the H–point of the bulk Brillouin zone of Te,\(^8,10,24\) as shown schematically in Fig. 2d. The six bands closest to the Fermi level within the probe photon energy range are shown, which include three successive valence bands (VBs) and two conduction bands (CBs). The uppermost two VBs \((H_4\) and \(H_5\)) are spin-polarized (non-degenerate) while the lower VB \((H_6^{VB})\) and the lowest CB \((H_6^{CB})\) are Rashba-like 2-fold
spin-degenerate and protected by the screw symmetry of the helices.\textsuperscript{8-10} The H\textsubscript{6} CB minimum has been proposed to be a Weyl node crossing.\textsuperscript{10} The intrinsic large SOI causes a camelback feature in the top $H_4$ VB along $H$–$K$ direction, showing a weakly indirect band gap in Te. In our experiment, the pump pulse of photon energy of 1.51 eV generates hot electrons and holes at different bands and these carriers are rapidly thermalized to their respective band minima through a rapid cascade of optical phonon emission. The time-delayed mid-IR probe pulse interrogates the occupation of each band with photoexcited carriers through monitoring the change in the reflectivity at the specific energies, which define the interband electronic transitions between the various bands (see vertical arrows). According to the schematic band diagram shown in Fig. 2d, the energies of these three optical transitions determined by fittings nearly match the energy of each band as predicted by theory.

The lowest energy transition $H_4 \rightarrow H_{6CB}^*$ with $E \perp c$ at longer (100 ps) delay is $E_1^\perp = 0.363 \pm 0.002$ eV, which is almost identical with the lowest energy transition with $E \parallel c$, i.e., $E_1^\parallel = 0.366 \pm 0.002$ eV. Although both of these transitions looks direct in nature and are nearly identical in energy, a weaker response (approximately one-third weaker) is observed with $E \parallel c$ at identical applied fluences, which is mainly caused by the higher reflectivity $R_0$ of the sample with $E \parallel c$ as compared to the reflectivity with $E \perp c$.\textsuperscript{34} Based on our observations, we do not see any evidence of a forbidden transition nor an indirect transition with $E \parallel c$ as discussed in previous works.\textsuperscript{18, 34} The transition energy near the fundamental gap $E_1^\parallel$ is $\sim 30$ meV larger than the previously measured band gap of bulk Te samples using linear optical absorption measurements.\textsuperscript{34, 40, 46} We expect that this increase in the absorption-edge or optical gap is caused by the Moss-Burstein shift of the Fermi energy below the maximum at $H_4$ in our naturally $p$-doped samples, as indicated in Fig. 2d. Prior Hall measurements in similar nanosheets have indicated a free hole density of $\sim 5 \times 10^{18}$ cm\textsuperscript{-3}.\textsuperscript{15} The optical transitions between $H_5 \rightarrow H_{6CB}^*$ is observable only with $E \parallel c$ and totally absent with $E \perp c$, consistent with the expected dipole allowed transition between these two states.\textsuperscript{47} The transition energy at longer delay is estimated to be $E_2^\parallel = 0.448 \pm 0.005$ eV, so that the energy separation between the Fermi level in the $H_4$ valence band and the $H_5$ valence band, we calculate $E_2^\parallel - E_1^\perp = 0.085$ eV. If we include the 30 meV doping-induced Fermi energy shift for the $H_4$ band, we find the splitting between the $H_4$ and $H_5$ band edges to be $\Delta E = 0.115$ eV, which coincides with the 11-micron hole absorption band, previously measured in a semi-insulating bulk single crystal of Te.\textsuperscript{35, 48}

The agreement between our optical transitions and their polarization dependence is strongly consistent with expected band calculations. In addition to the direct transitions between uppermost VBs
and the lowest CB, there is an indication of a higher energy transitions at around $E_{3}^{\parallel,\perp} = 0.75 \pm 0.005$ eV and the transition is weakly sensitive to polarizations. The fact that the TR signal is nearly one order of magnitude weaker than the near band-edge transition suggests that this transition might be indirect in k-space. Indeed, if we look at the band structure shown in Fig. 2d, the valence band $H_{6}^{VB}$ is doubly spin-degenerate in which one of the spin-states shows a maximum outside $k_{x} = 0$ at the H-point before extending to the Weyl node. Therefore, such transitions most likely to occur between the band-edge at $H_{6}^{VB}$ and the lowest conduction band $H_{6}^{CB}$. One thing to note here is that the transition energy $E_{3}^{\parallel,\perp}$ falls right in the inaccessible gap of our photon source, i.e., $0.72 - 0.8$ eV, which adds a bit of uncertainty in estimating the transition energy.

We also observed a higher lying transition at $E_{4}^{\parallel,\perp} \sim 1.25 \pm 0.005$ eV, which is nearly four-times the fundamental gap. The TR response of this transition is relatively stronger (more than twice larger in magnitude) than $E_{3}^{\parallel,\perp}$ response at longer delays but still much weaker than the response from band-edge transitions. Due to limitations of the spectral range of the probe pulse, only one-half of the derivative-like line shape is accessible by our experiment, which causes uncertainties to extract the precise energy and polarization anisotropy of this transition. Since the conduction bands above $H_{6}^{CB}$ and valence bands below $H_{6}^{VB}$ at the H-point are far apart, the next higher energy transition at the H-point beyond $E_{3}^{\parallel,\perp}$ is not accessible with our probe beam. Based on the extended band-structure of Te around all high symmetry points in the Brillouin zone, we find that there is only one transition possible at the L-point that matches with $E_{4}^{\parallel,\perp}$. Therefore, we suspect that the transition $E_{4}^{\parallel,\perp}$ is caused by a quasi-direct transition at the L-point.

Estimation of band-edge parameters. It is important to note that the hydrothermally-prepared material is highly p-type, and so the lowest observed optical transition is between the Fermi level in the highest lying valence band to the bottom of the lowest conduction band. The TR lineshapes result from changes in the real and imaginary part of the index of refraction caused by the presence of the photoexcited electrons and holes. The additional holes cause a further slight downshift of the Fermi energy near the top of the $H_{4}$ VB maximum. This changes the energy onset of the absorption for optical transitions from the Fermi level in $H_{4}$ band to the lowest CB $H_{6}^{CB}$. We calculate this change in the absorption coefficient (see Methods Section), which causes a corresponding change in the real part of the index of refraction calculated using a Kramers-Kronig transformation. The free parameters in this calculation are the density of the doped hole gas in $H_{4}$ band, the density of photoexcited carriers (electron-hole pairs), the temperature of the electrons and holes, and the fundamental gap energy $E_{g1}(H_{4} \rightarrow H_{6}^{CB})$. We consider
parabolic bands with electron and hole effective masses, $0.6 \cdot m_e$ and $0.4 \cdot m_e$, respectively ($m_e$: rest electron mass) for our model calculations. The resulting Fermi energy is relatively small because of the substantial degeneracy of the valence ($H_4$) and conduction ($H_6^{CB}$) bands, i.e., 12 and 24, respectively, in this complex band structure. Figure 3 shows TR spectra (black circles) measured with $E \perp c$ at three different delay times around low-energy regions, which are well reproduced by our model calculations. The blue solid lines overlapped on each spectrum with scales on the right show a decrease in the absorption (photoinduced bleaching) due to the pump laser excitation. Best fitting of the spectra to the model yields the doped hole gas density to be $N_d \sim 2 \times 10^{18}$ cm$^{-3}$, which implies a Fermi energy of $E_f \sim 30$ meV, and a fundamental gap between minima of $H_4$ and $H_6^{CB}$ of $E_g \sim 0.32 \pm 0.005$ eV. Our estimated doping density agrees fairly well with those obtained by Hall measurements on similar nanosheets. The photoexcited carrier density (both electrons and holes) at the band edge reaches to $N_{eh} \sim 1 \times 10^{18}$ cm$^{-3}$ at a delay time of 10 ps. These parameters result in a zero crossing of the lineshape at the minimum of the absorption change $\Delta \alpha$ (right scale in Fig. 3) at 0.368 eV, which matches closely with $E_{1L}$ and shows a good consistency check in the modeling. All the band parameters obtained from the model fittings are tabulated in the Supplemental Information. The estimated fundamental band gap is consistent with previous steady-state optical measurements performed at low-temperatures on moderately doped bulk samples.
Fig. 3. Modeling the transient reflectance spectra of Te nanosheets. Typical derivative-like transient reflectance spectra (black filled circles) around the fundamental gap region measured with the $E \perp c$ configuration of the probe pulse at three different pump-probe delay times. Each spectrum is well reproduced using a simple model (red lines), which accounts the change in absorption induced by pump pulses due to state filling and subsequently a change in real part of refractive index through Kramers-Kronig transformation. The calculated change in absorption $\Delta \alpha$, normalized by the peak values for clarity, at respective delay times are also superimposed with scales on the right (blue lines). Overall, the model captures main feature of the spectra and extracts important band parameters such as band gap and Fermi energy.

**Dynamic evolution of band-edge anisotropy.** Figure 4a,b shows a series of selected TR spectra recorded at different delay times for both orthogonal polarizations around the low-energy region. Each spectrum is fitted using Eq. (1) and superimposed onto the spectra with dashed red lines. As described earlier the spectra with $E \perp c$ fit well with a single transition energy ($n = 1$) while the spectra with $E \parallel c$ fit well
with a two transition energies, i.e., \( n = 2 \) (eq. (1)), close to each other but phase shifted by \( 180^\circ \). Corresponding moduli (these are equivalent to absorption bands) of the spectra calculated from each corresponding fit are also shown in Fig. 4c,d. We can immediately notice the time evolution of the peak position, which corresponds to the transition energy, with respect to the probe pulse delay for both polarizations. The transition energies extracted from the fits or peak of each modulus are plotted as a function of delay in Fig. 4e. The lowest transition energy with \( E \perp c \) remains steady at the ground-state value of \( E_1^\parallel = 0.36 \text{ eV} \) except a minor down-shift (\( \sim 3 \text{ meV} \)) within 2 ps. Such an abrupt down-shift of band-gap is attributed to the band-gap renormalization, which generally occurs in semiconductors upon photoexcitation due to many-body effects arising from the hot and dense electron-hole plasma. The lowest energy transition with \( E \parallel c \), however, is shifted by \( \sim 20 \text{ meV} \) higher than \( E_1^\parallel \) near time zero. The next higher energy \( E_2^\parallel \) transition between \( H_5 \rightarrow H_6^{CB} \) with \( E \parallel c \), which is dipole forbidden with \( E \perp c \), is red-shifted by nearly 10 meV near time zero. Interestingly, both of these transitions with \( E \parallel c \) gradually return back to their respective ground state transitions within \( \sim 30 \text{ ps} \). The transient recovery of these transitions is further quantified by plotting the delay dependence of energy difference near the first and second band-edge regions, i.e., \( E_2^\parallel - E_1^\parallel \) and \( E_2^\parallel - E_1^\perp \), respectively, as well as spin-split gap, i.e., \( E_2^\parallel - E_1^\parallel \) (see the inset of Fig. 4e). The energy relaxation occurs on the same time scale (i.e., \( \sim 30 \text{ ps} \)) as the carrier decay time around the low-energy region (Fig. 5a, discussed later), suggesting strong correlation of band-edge shifts with the band occupation.
Fig. 4. Dynamic evolution of anisotropic optical transitions in photoexcited Te nanosheets. **a, b** Series of selected TR spectra (blue lines) recorded at different pump-probe delay times for both $E \perp c$ and $E \parallel c$ polarizations. Dashed red lines are model fits of each corresponding spectrum. **c, d** Moduli of each corresponding fit for both polarizations. Vertical dashed grey lines are guide to eyes to indicate the systematic shift of peak position. **e** Transition energies $E_1 \perp$, $E_1 \parallel$, and $E_2 \parallel$ extracted from the fits and plotted as a function of delay for both polarizations. Error bars are estimated from the least square fitting procedure. While the $E_1 \perp$ remains mostly stable over a long delay, the $E_1 \parallel$, and $E_2 \parallel$ undergo gradual blue and redshifts as delay progresses before they remain steady after ~ 30 ps). The inset shows the time evolution of anisotropic spectral shifts, as quantified by $E_1 \parallel - E_1 \perp$ and $E_2 \parallel - E_1 \parallel$ for fundamental and higher energy band gap anisotropy and $E_2 \parallel - E_1 \parallel$ for the gap between uppermost valence bands excluding the doping induced Fermi energy shift. Superimposed dashed lines on each curve are exponential fits for a guide to the eye. The shaded region is shown to indicate the static region. **f** Ground-state and photoinduced band structure (exaggerated energy scales) around the H-point near the band-edge, showing photoinduced splitting $\Delta E = E_1 \parallel - E_1 \perp$ of $H_6^{CB}$ band and narrowing of uppermost $H_4$ and $H_5$ VBs. Involved optical transitions are indicated by vertical arrows.

The physical origin of this dynamic shift of bands in the first 30 ps after the pump pulse is non-trivial. Because the shifts are both positive and negative for different transitions, it is not possible to explain the shifts due to the usual ultrafast processes including any excitonic, many body or band filling
effects. Excitonic interactions are safely ruled out in our samples due to the very low exciton binding energy \( E_b \approx 0.5 \text{ meV} \ll E_g \) of bulk Te.\(^{51}\) An ultrafast band-gap collapse upon high density (>1% of valence electrons, or \( \sim 10^{21} \text{ cm}^{-3} \)) excitation is predicted in Te,\(^{52}\) which is not possible here due to our low density excitation (\( \sim 10^{18} \text{ cm}^{-3} \)). Therefore, we propose that these dynamic shifts in the first 30 ps arise due to lifting of the \( H_6^{CB} \) spin degeneracy by photoinduced lattice strain generation. Relaxation of these strains must be correlated with decay of photoexcited carriers in the Te crystal. Recent theoretical studies have also predicted various possibilities of band-structure modifications due to uniaxial, hydrostatic or shear stress in a Te crystal.\(^{9, 30}\) Under uniform or uniaxial strain, both \( H_6^{CB} \) and \( H_4 \) bands move vertically, either decreases the gap (for compressive strain) or widens (for tensile strain), but both preserve the \( H_6^{CB} \) band degeneracy. Shear strain, however, affects both bands but also lifts the degeneracy of the \( H_6^{CB} \) band by breaking the screw symmetry of Te helix.\(^{9}\) This suggests that shear strain contributes dominantly in our experiment because the band gap with \( E \perp c \) (i.e., \( E_1^\perp \) transition) remains unchanged upon photoexcitation. Additionally, we didn’t observe any significant changes in the induced band-edge shift by rotating the pump polarization either parallel or perpendicular to c-axis, which is in contrast to the uniaxial strain effect in the anisotropic crystal of Te.\(^{9, 53}\) Furthermore, due to the induced shear strain, it is expected to change the spin-split gap between \( H_4 \) and \( H_5 \) VBs due to the resulting change of the spin-orbit coupling parameter,\(^{54}\) which is also observed in our experiment. These likely effects of strain resulting from photoexcitation are schematically shown in Fig. 4f, which explains fairly well our observations. The maximum splitting, \( i.e., E_1^\parallel - E_1^\perp \), of the \( H_6^{CB} \) band near the time zero turns out to be \( \sim 20 \text{ meV} \) while the spin-split gap between uppermost VBs, \( i.e., E_2^\parallel - E_1^\parallel \), is reduced by \( \sim 30 \text{ meV} \). Note that the exact evaluation of the spin-split gap is hindered by the lack of well-resolved transitions from \( H_5 \) to the closely spaced \( H_6^{CB} \) split bands. The splitting of the CB results in a strong line broadening of the \( E_2^\parallel \) TR spectra as compared to the spectrum of \( E_1^\parallel \) transition at early times, as indicated by green and red dashed fits in Fig. 4d. The shifts in both transitions gradually return to ground-state values as the majority of photoexcited carriers relaxes to the ground-state within first \( \sim 30 \text{ ps} \), suggesting strong interaction of strain induced band modifications with photoexcited carriers.

The origin of the photoinduced strain generation in our samples can be from three possible mechanisms: thermoelastic, electron-acoustic deformation potential, and inverse piezoelectric effect (IPE). Both the thermoelastic and deformation potential mechanisms induce negligibly small stresses (less than \( 10^{-3} \) GPa, see Supplemental Information) due to the small excitation density used in our experiment. Such stress values are too small to induce the tens of meV band gap shifts\(^{53}\) that we observed in our
samples. Therefore, we believe that the inverse piezoelectric effect (IPE) is the most likely mechanism to cause band modifications through shear strain generation in our samples. We estimate from the measured splitting of $H_6^{CB}$ CBs, an induced shear strain on the order of $10^{-3}$. Note that IPE has been observed previously in various piezoelectric semiconductors\textsuperscript{55,56} and is also expected in our samples due to the fact that Te is an anisotropic piezoelectric crystal with a reasonably high piezoelectric coefficient\textsuperscript{32,33,57} and is also predicted to show in-plane spontaneous charge polarization (ferroelectricity).\textsuperscript{58} Upon photoexcitation by the pump pulse, photogenerated electrons and holes screen the built-in electric field in the film (most likely at the surface)\textsuperscript{33} that induces a strain wave through IPE. The induced strain relaxes as excited carriers decay because the screening slowly vanishes. Direct evidence of the strain wave propagation the film can be observed through the periodic change of the TR signal due to the interference between the strain wave and the probing laser pulse.\textsuperscript{59,60} We have observed a weak oscillatory component in our TR signal corresponding to the coherent longitudinal acoustic phonons (CLAP), \textit{i.e.}, sound wave propagation in the film, which supports photoinduced strain generation in our samples. (see Supporting Information) The velocity or the oscillation frequency of the CLAP deviates from the in-plane or out of plane modes, which may be an indication of shear strain contributions along with other modes in our samples.

**Polarization and energy dependent carrier dynamics.** Since we observe the transient response of the polarized TR spectra, it is interesting to look at polarization dependent carrier decay processes associated with these various bands transitions as the photoexcited carriers relax to their ground state. Representative polarized time decays from the two low and high energy regimes are shown in Fig. 5a,b.. Near the band gap region (see Fig. 5a), almost all of the TR response recovers exponentially within first 30 ps followed by a very weak (nearly 2-orders of magnitude lower than the peak) long-lived (> 1 ns) residual signal. Around the high-energy regime (see Fig. 5b), which falls around the direct gap at the L-point, the decay profiles display an initial ultrafast decay of a fraction of the signal followed by a long exponential recovery of the majority of the signal at later times. In order to quantify the overall decay behavior around the low and high energy regimes, each time trace is fitted using multi-exponential functions convoluted with a Gaussian response function: \textsuperscript{61}

$$\Delta R/R_0 (t) = \sum_{i=1,2,3} c_i \cdot \sigma \cdot \exp\left[(\sigma/2\tau_i)^2 - (t/\tau_i)\right] \cdot [1 - erf\left((\sigma/2\tau_i) - (t/\sigma)\right)],$$

(2)

where $c_i$ is the amplitude with decay time constant of $\tau_i$ of the $i^{th}$ exponential term and $\sigma$ is full width half maximum of the pump laser pulse ($\sigma = 200$ fs). A least square fitting to Eq. (2), as shown by dashed red lines in Fig. 5a,b, estimates the decay time constants $\tau_i$ of each $i^{th}$ decay channel at different bands. Near the low-energy region (Fig. 5a), the initial fast and slow decay constants are $\tau_1 \sim 5 \pm 1$ ps and
$\tau_2^\perp \sim 20 \pm 1$ ps, respectively for $E \perp c$ and both decay times are twice longer for $E \parallel c$, i.e., $\tau_1^\parallel \sim 9$ ps and $\tau_2^\parallel \sim 36$ ps, respectively. In addition, there is a small residual signal (two orders of magnitude smaller than the peak value) that exists for both polarizations, which slowly decays within $\tau_3^\perp \approx \tau_3^\parallel \sim 2$ ns. Around the high-energy region (Fig. 5b), only a fraction ($\sim 30\%$) of the peak intensity decays abruptly within a sub-ps ($\tau_1^\perp \sim 0.8 \pm 0.1$ ps) time after the excitation pulse for $E \perp c$ and is nearly 10-times slower for $E \parallel c$. The majority of the signal decays slowly with a decay time in the order of $\sim 1$ ns for both polarizations.

Fig. 5. Probe polarization and energy dependent carrier dynamics in Te nanosheets. Representative polarization resolved transient reflectance (TR) $\Delta R/R_0$ traces of Te samples around the fundamental band-edge a and higher energy transition region b. Dashed red lines are the multi-exponential fits of each corresponding data over a long delay range, as described in the main text. Insets show the initial decay responses of each corresponding trace. Around band-edge region, majority of the TR signal relaxes within first 30 ps due to ultrafast intraband thermalization followed by interband recombination. Around the higher energy transition, only a fraction of the maximum TR signal decays rapidly predominantly by intervalley scattering accompanied by intraband thermalization, while the rest of the signal recovers on the order of a nanosecond due to interband recombination. c Schematic drawing of carrier excitation and relaxation processes within extended bulk band structure of Te around high symmetry points in the Brillouin zone. Pump excitation is indicated by vertical red arrows and probe excitation is shown by vertical purple arrows for different regions of the probe energies. Intraband carrier thermalization by phonon emission is shown with curved arrows. Inter-valley forward scattering and backscattering are symbolized by solid and dotted green arrows, respectively.

The physical origin of the TR decay response observed in our experiment can be understood from the band diagram of bulk Te, as shown schematically in Fig. 5c. Immediately after pump excitation
(vertical red arrows), the TR response decreases abruptly due to absorption bleaching through state filling of hot electrons and holes in their respective bands before they establish a Fermi Dirac distribution within a few femtoseconds by carrier-carrier scattering. Subsequent recovery of the TR response occurs through basic carrier relaxation processes that may vary at different bands due to the different scattering channels involved. Near the low-energy region, the TR signal initially decays rapidly as hot carriers are rapidly thermalized to the lattice temperature through a cascade of optical phonon emissions and carrier-carrier scattering with the cold and dense hole gas in the VB while relaxing to the band minima, as indicated by curved arrows in Fig. 5c. The early transient is mainly dominated by the thermalization of hot holes due to efficient scattering with the cold degenerate hole gas due to their higher effective mass as compared to the electron mass. Therefore, the initial fast decay component of $\tau_1 \sim 5$ ps corresponds to an upper bound to the effective scattering time for a hole density of $N_d$. The subsequent slower decay time of $\tau_2 \sim 20$ ps is attributed to the interband carrier recombination time around the fundamental gap. Since our samples are thinner than the typical laser penetration depth $l_{IR}$ in Te around the IR-region ($l_{IR} \sim 50$ nm), long-range carrier diffusion process does not contribute to the decay response. The weak residual signal (just 5% of the peak) observed after the initial carrier recombination persists over a ns delay and is attributed to a constant supply of long-lived carriers from higher lying bands through phonon-assisted intervalley processes. Note that the initial rapid decay time for $E \parallel c$ is nearly twice slower than that for $E \perp c$, as shown more clearly in the insets of Fig. 5a. This observation is directly related to the anisotropic characteristics of Te. The electrical conductivity of bulk Te, including the hole mobility and scattering time, have been found to be larger ($\sim 1.2 - 2.3$ times larger) along the c-axis than that of perpendicular to the c-axis. In particular, the free carrier scattering time parallel to the c-axis is measured to be 3-times longer than that of perpendicular to the c-axis due to stronger coupling of polar optical scattering along the perpendicular to the c-axis, which is considered the main scattering process in $p$-doped Te samples. Such an anisotropic carrier scattering process is nicely reflected in the carrier decay dynamics of our samples, which could be also relevant in other anisotropic materials.

Around the high-energy region ($\sim 1.2$ eV), the carrier decay dynamics is largely associated with the direct transition near the band-edge at the L-point and, therefore, involves fundamentally different scattering processes. Due to closely spaced multiple conduction bands at the neighboring A-valley (see Fig. 5c), intervalley coupling of hot carriers between L- and A-valley is highly favorable at early times. Photoexcited hot electrons at the L-valley will scatter rapidly with the A-valley via deformation potential scattering followed by return scattering to the L-valley, as indicated by green solid and dotted arrows, respectively, in Fig. 5c. The TR response for $E \perp c$ displays sharp transient within a sub-ps time ($\tau_1 \sim$
0.8 ps) followed by slower recovery of the signal ($\tau_{1/2} \sim 5$ ps) until it reaches thermal equilibrium with the lattice (quasi-steady state regime). We attribute the early sub-ps decay time to an upper limit of average intervalley scattering time $\tau_{iv}$ between the L- and A-valleys and subsequent slower decay constant to the intraband cooling time within the L-valley, which is nearly identical with the band-edge thermalization time at the H-point. Our data of $\tau_{iv} \sim 0.8$ ps is comparable with the data obtained from other semiconductors such as GaAs.$^{64}$ Since the intervalley return scattering time is much longer than forward scattering time due to the lower density of states at the A-valley, the second decay component $\tau_{2/4}$ may involve both intervalley return scattering as well as intraband cooling processes. The TR signal after cooling of carriers, i.e., the degree of state filling of thermalized carriers at the band edge, reduces only marginally (only $\sim 30 \%$ of the peak), which is likely due to the reduced density of optically coupled state filling at the band minima due to dominant intervalley forward scattering. The ultrafast intervalley process creates a long-lived reservoir of carriers at the A-valley, which eventually bleed back to the band minima at the H-valley. This extraction time corresponds to the long-lived decay ($\tau_{3/4} \sim 1$ ns) seen for the H-valley transition. We note that the TR response for $E \parallel c$ is markedly different at early times but qualitatively resembles the subsequent long-lived decay response due to the constant feeding of carriers to H-valley (see Fig. 5b). The early decay is dominated by the much slower ($\tau_{1/4} \sim 8$ ps) carrier thermalization rate, which is again, as we discussed earlier, supported by the arguments of higher mobility and scattering lifetime of free carriers along the c-axis. This observation of longer early decay response suggests intervalley scattering is effectively suppressed with $E \parallel c$ and hints also possible consequences of photoinduced band modification even in the higher lying bands.

**Discussion**

The nature of interband optical transitions in Te is not trivial due to the unique spin texture and energy dispersion of the uppermost valence bands and the lowest conduction band. For transitions between the highest lying valence band $H_4$ to the lowest $H_6^{CB}$ conduction band, group theory indicates that optical transitions are only allowed for $E \perp c$ and forbidden for $E \parallel c$. Most previous works have looked at direct absorption in a bulk crystal and shown a direct transition with $E \perp c$, but also that the transition energy depends on temperature and the polarization of the incident laser beam.$^{34, 35, 40, 46}$ Transient reflectivity at long times should be comparable to absorption measurements assuming the initially hot carriers have thermalized close to the lattice temperature. Our assignments of the $H_4 \rightarrow H_6^{CB} (E \perp c)$ and $H_5 \rightarrow H_6^{CB} (E \parallel c)$ transitions agree well with the bulk absorption measurements at low temperature.$^{18, 40}$ However, detailed analysis of $E \parallel c$ and $E \perp c$ TR spectra suggests that at late times the ground state
exhibits direct degenerate transitions for both polarizations within experimental error. While such a result has been seen by others,\textsuperscript{37,40} it is inconsistent with the group theory result that the $E \parallel c$ transition should be forbidden.\textsuperscript{34} This disagreement may reflect the complicated spin texture and energy dispersion of the uppermost $H_5$ VB, and the Weyl node crossing of the $H_6^{CB}$ CB. The lifting of the degeneracy at the CB minimum at early times may also provide insight into the nature of these polarized optical transitions.

The polarized TR measurements also indicate an indirect transition around 0.7 eV, which we have attributed to optical transitions between the doubly degenerate $H_6^{VB}$ to $H_6^{CB}$ which is seen for both polarizations. The weakness of this broad transition suggests that it is potentially $k$-space indirect because of the complicated dispersion of the higher lying $H_6^{VB}$ VB away from the H point. This has been predicted theoretically but never been observed experimentally. The highest energy transition observed in these TR measurements is near $\sim 1.2$ eV which we have identified with a direct transition between the VB and CB at the L point in the Brillouin zone. More importantly these highest energy transitions appear to be long-lived suggesting they can be a source for charged carriers. All of these observations are potentially important in the design of efficient thermoelectric and electronic devices due to the complexity of the polarization effects and their dynamics.

The most interesting result of these measurements is the unusual dynamics of the $H_4$ and $H_5$ VBs and the $H_6^{CB}$ CB. In the first 30 ps when the vast majority of the charged carriers decay, our results indicate that the spin-split gap between the $H_4$ and $H_5$ VB decreases by 10 meV at $t = 0$ ps, but recovers within 30 ps. Similarly, the degeneracy of the two $H_6^{CB}$ states is lifted by 20 meV at $t = 0$ ps but also recovers within 30 ps. We argue that this unusual dynamics is a direct consequence of photoinduced band modifications caused by internal shear strain generation in the Te crystal through the inverse piezoelectric effects, which lifts the degeneracy of $H_6^{CB}$ and reduces the spin-split gap of the uppermost VBs ($H_4$ and $H_5$). As soon as the majority of the photoexcited electrons and holes recombine, the piezoelectric strain relaxes and the band-edge modulation recovers back to ground state values. This observation is quite different than is usually observed in uniaxial or hydrostatic strain\textsuperscript{9,53,54} where the band gap increases or decreases but does not lift the degeneracy of the $H_6^{CB}$. However, the results described here are similar to recent work\textsuperscript{30} of symmetry breaking of Te helices by alloying with Se that produces internal strain via lattice deformation within each helix. This suggests that optical excitation can induce distortion in the Te helices which is sufficient to produce measurable shift in the frontier VBs as well as lift degeneracies in the $H_6$ bands. Similar strains have been predicted to induce a strong topological insulator or Weyl semimetal phase in Te when screw symmetry is broken and band inversion is created above a critical strain $\sim 5.5\%$.\textsuperscript{9,30} This suggests that light-matter interactions can offer an alternative pathway for
manipulating trivial to topological electronic phases in Te, opening new perspectives for novel spintronic devices.

The consequence of anisotropic optical transitions is also reflected in the polarization dependent carrier decay dynamics. Near the band gap region, the $E \parallel c$ time decay is twice as slow as $E \perp c$. Such anisotropy is also seen in tellurium’s transport properties. In particular, mobility measurements indicate that the free carrier scattering time perpendicular to the c-axis is 3-times faster than along the c-axis due to higher coupling of polar optical scattering,\textsuperscript{18, 63} which compares favorably with our observations. Similar anisotropic behavior is seen at high energies (~1 eV) where the initial ultrafast sub-picosecond decay is only observed for $E \perp c$ but not seen for $E \parallel c$. Direct intervalley scattering between the $L^{CB}$ and A-valleys for electrons as well as $L^{VB}$ and $H^{VB}_6$ bands for holes is favorable in Te due to the presence of multivalley isoenergetic states at the A-point for electrons and $H^{CB}_6$ VBs for holes. This polarization dependent behavior suggests that not only the interband transition but also intervalley process are sensitive to polarization configurations in Te, which is equally relevant for other anisotropic materials.

The long-lived dynamics observed in these TR measurements is also notable. The vast majority of the carriers at the band edge at $t = 0$ ps decay within 30 ps, but there is a persistent very small (usually only 1% of the initial carrier density) which is observed over 1 ns. At higher energies, the initial rapid decays are only fractionally, followed by a long-lived decay approaching 1 ns. We have interpreted this result as evidence for some of the electrons and holes photoexcited by the 1.5 eV pump pulse scattering into remote L- or A-valleys which then provides a long-lived source of carriers to the lowest band edge at the H point. When the probe pulse is tuned to 1.0 to 1.2 eV we anticipate that it is monitoring the population of the L or A valleys. Only a small fraction of the initially excited carriers scatter to these valleys. The long decays observed at these energies suggest that carriers populate these remote valleys and only gradually scatter back to the lower lying states at the H point. The understanding of the polarization sensitive excitation and scattering effects observed in these measurements will require more study in the future.

**Summary and Conclusions**

We have made extensive measurements of polarized transient reflectivity dynamics over a wide range of energies from the band edge to four times the band edge. Modeling of the derivative like responses indicates a number of polarization sensitive optical transitions over this entire range of energies. Specifically, we have observed the $H_4 \rightarrow H^{CB}_6$, $H_5 \rightarrow H^{CB}_6$ and $H^{VB}_6 \rightarrow H^{CB}_6$ transitions between the VB and CB at energies and symmetries which are consistent with band structure calculations. At the highest
energy, we observe a potential quasi-direct transition, which is associated with L point. The complex
dynamics show rapid recombination of the majority of the carriers at the band edge within 30 ps, followed
by a slow feeding of carriers from remote valleys (presumably from the L or A valleys) over the following
nanoseconds. The existence of this long-lived source of photoexcited carriers is observed in the dynamics
associated with the L valley near $\sim 1.2$ eV. More importantly, within the first 30 ps decay we have
spectroscopic evidence of photoinduced strains that cause an anisotropic shift in the $H_4$ and $H_5$ valence
bands and a lifting of the Weyl node degeneracy of the $H_6$ CB. These strains clearly relax as the carriers
decay away and are small after 30 ps. These results provide the first time-resolved and polarization-
resolved data of electronic structure and carrier decay dynamics over an extended band-edge region of Te
measured by ultrafast probes, which are crucial for designing Te-based novel optoelectronic,
thermoelectric and spintronic devices.
Methods

Growth of Te nanosheets. Te nanosheet samples were grown chemically through the reduction of sodium tellurite (Na$_2$TeO$_3$) by hydrazine hydrate (N$_2$H$_4$) in an alkaline solution at temperatures from 160 – 200°C with the presence of crystal-face-blocking ligand polyvinylpyrrrolidone (PVD).[15] The hydrophilic Te nanosheets were transferred to thermally oxidized Si substrates by the Langmuir–Blodgett assembly process.

Sample characterization. Surface morphology and thickness of Te sheets were measured by using atomic force microscope (AFM). Measurements were conducted in air on a Veeco AFM using gold (Au) coated platinum (Pt) cantilevers operating in tapping mode. Raman spectroscopy was applied to characterize sample quality and crystal orientation. The measurements were performed using a home-built Raman microscope with 632.8 nm laser excitation in the backscattering configuration under ambient condition. Te sample was rotated with respect to the laser polarizations in order to identify the crystal c-axis and characterize polarization dependent Raman spectra. A 100 × objective was used to focus the incident beam and collect the scattered signal and then dispersed by 1800 g/mm grating after the resonant scattered laser light is removed using a double subtractive mode spectrometer. The Raman signal is measured with a spectral resolution of 1 cm$^{-1}$. The lowest frequency observable is 50 cm$^{-1}$. Laser power was maintained around 100 μW during the measurements to minimize laser-heating effect in our samples.

Transient reflectance spectroscopy. Ultrafast pump-probe TR measurements were performed based on a Ti:sapphire oscillator which produces 200 fs pump pulses at a central wavelength of 800 nm with 80 MHz repetition rate and an average power of 4 W. The majority (80%) of the laser beam was used to pump an optical parametric oscillator (OPO), which generates signal (0.72 – 1.2 eV) and idler (0.3 to 0.8 eV) photons, which can be tuned continuously over a wide range. All measurements were performed using 820 nm (hω$_p$ = 1.51 eV) as the pump pulse and both signal and idler outputs as probe pulses, respectively, as illustrated in Fig. 2a. The polarization of the probe pulses with respect to the crystal c-axis is controlled using a CaF$_2$ double Fresnel rhomb on the probe beam path. The probe pulses are delayed in time with respect to the pump pulses by using a motorized linear translation stage. The pump and probe beams are spatially overlapped on a single Te sheet using a 40 × protected silver reflective objective with the help of CCD camera, and the reflected beams are directed to the liquid nitrogen cooled InSb detector. The pump beam is filtered out during the TR measurements using a long pass filter. The pump-induced signal is collected with a lock-in amplifier phase-locked to an optical chopper that modulates the pump
beam at a frequency of 1 kHz. The focused spot size of both pump and probe beams is nearly identical, \( \approx 2 \mu m \) in diameter. An average pump fluence of \( \approx 0.5 - 1 \text{ mJ/cm}^2 \) (still well below the damage threshold or low excitation regime in bulk Te)\(^{65} \) was used throughout the experiments, while the probe fluence was kept nearly one order of magnitude lower.

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**Author contributions**

G.J. and L.M.S. conceived the study. Y.X.W., G.Q, W.Z.W., and P.D.Y. synthesized Te nanosheet samples. G.J. characterized the samples, performed TRS measurements, data analysis, figure planning, and draft preparation. I.A.S. helped in the micro-Raman measurements. S.L. helped in the TRS experiments. S.L. modeled the TRS spectra with inputs from G.J., L.M.S., and H.E.J. G.J. and L.M.S. wrote the manuscript. All coauthors contributed to the discussion of results and commented on the manuscript.

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The authors declare no competing financial interests.
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Supplementary Information

Ultrafast Band-edge Optical Anisotropy and Carrier Dynamics in Te Nanosheets

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Supplementary Note 1: Transient reflectance spectroscopy (TRS) at 300 K

A. Optical transitions

Supplementary Figure 1a displays a false color map of the 300 K TR spectra measured over a wide spectral region (0.3 – 1.2 eV) for the probe polarized parallel (E \parallel c) and perpendicular (E \perp c) to the c-axis. Overall, the TRS map exhibits strong anti-symmetric features around low-energy (0.3 – 0.5 eV) and high-energy (0.8 – 1.2 eV) regions and a relatively weaker and broader signal near the mid-energy (0.5 – 0.8 eV) region, corresponding to a series of interband optical transitions. The map also shows that the strong features remain essentially unchanged in shape with time except for their magnitudes, suggesting only a weak perturbation of the transition response by the carrier thermalization process. These features are more apparent in Supplementary Figure 1b where the spectral slices at 50 ps delay from each polarization are plotted (blue circles). The derivative-like spectral features of the transient signal around the low- and high-energy regions exhibit significant differences for the two polarizations, while the broad feature in the mid-energies also displays some sensitivity to polarizations. With E \parallel c, a nearly overlapped additional feature is observed at \sim 0.44 eV, which is not present with E \perp c, suggesting the polarization sensitive optical absorption in the Te samples.

It is known that the TR response is related to the perturbation of the dielectric function of the material induced by photoexcitation of charged carriers. For the Lorentzian form of the dielectric function under low-field modulation with the parabolic band approximation, TR spectra around the band-edge regions can be analyzed by using a derivative Lorentzian line-shape functional form appropriate for excitonic transitions,

\[ \frac{\Delta R}{R_0}(E) \approx \sum_{j=1}^{n} \text{Re} \left[ A_j e^{i\varphi_j} \left( E - E_j + i\Gamma_j \right)^{-2} \right] , \]  

where \( n \) represents the number of spectral functions for the possible interband transitions involved, \( E \) is the probe photon energy, and \( A_j, \varphi_j, E_j, \) and \( \Gamma_j \) are the amplitude, phase, transition energy, and the energy broadening parameter of the \( j^{th} \) feature, respectively. In order to quantify each of these features and corresponding transition energies, the TRS spectra are fitted using Eq. (2), as shown with red dashed-lines in Supplementary Figure 1b. The spectra with E \perp c can be fitted by three resonances (\( n = 3 \)) while the spectra with E \parallel c can be fitted by four resonances (\( n = 4 \)). Moduli of the individual resonances, which have been obtained from Eq. (2), are also overlapped with minor vertical shifts for clarity (black solid lines in Supplementary Figure 1b). The values of the transition energies obtained from least square fitting are indicated by vertical dashed grey lines.
Now, we compare the transition energies of each \textit{j}^{th} feature with the detailed band structure around the H–point of the bulk Brillouin zone of Te\textsuperscript{2-4} as shown schematically in the main text. The lowest energy transition $H_4 \to H_6^{CB}$ with $E \perp c$ is $E_1^\perp = 0.34 \pm 0.002$ eV, which is nearly the same value as the low (10 K) temperature value shown in the main text. This behavior nicely corresponds with the peculiar temperature dependent absorption coefficient in Te previously observed.\textsuperscript{5} One can also see the lowest energy transition with $E \parallel c$, which is blue-shifted by $\sim 20$ meV to $E_1^{\parallel} = 0.36 \pm 0.002$ eV. Such a polarization anisotropy of optical transition at the band-gap remains unchanged over entire delays, in contrast to the strong modulation up to 30 ps observed at 10 K (see main text). The $E_1^\perp$ transition energy as well as the polarization anisotropy (\textit{i.e.}, the dichroism of the optical absorption edge) agree very well with previous results obtained by linear absorption measurements on degenerately p-doped Te samples at room temperature.\textsuperscript{5-7} The optical transition between $H_5 \to H_6^{CB}$ is observable only with $E \parallel c$ and totally absent with $E \perp c$, which is in agreement with low temperature measurements and consistent with the expected dipole allowed transition between these two states. The $H_5 \to H_6^{CB}$ transition energy is estimated to be $E_2^{\parallel} = 0.44 \pm 0.005$ eV, which is again nearly identical with the value measured at 10 K. The spin-split gap or the separation between the $H_4$ and the $H_5$ VBs turns out to be $E_2^{\parallel} - E_1^\perp = 100$ meV. This value, taking into account the doping-induced Fermi level shift, is nearly the same as the so-called 11-micron hole absorption band previously measured in a bulk single crystal of Te.\textsuperscript{8-9} The energy difference between the $E_2^{\parallel}$ transition and $E_1^{\parallel}$ transition decreases to $E_2^{\parallel} - E_1^{\parallel} = 80$ meV, which suggests not only the fundamental gap but also the gap between spin-split VBs is anisotropic at room temperature. In addition to the direct transitions between uppermost VBs and the lowest CB, there is an indication of a higher energy transition near $E_3^{\parallel,\perp} = 0.75 \pm 0.005$ eV with the lineshape sensitive to polarizations. Since the TR signal is nearly one order of magnitude weaker than the near band-edge transition, this transition might be indirect in k-space, as expected from the band structure.

We also observed a higher lying transition at $E_4^{\perp} \sim 1.16 \pm 0.005$ eV, which is blue shifted by 20 meV to $E_4^{\parallel} \sim 1.18 \pm 0.005$ eV. Due to limitations of the spectral range of the probe pulse, a full derivative-like line shape is not observed, which causes uncertainty in the precise energy transition. Nevertheless, the transition is clearly sensitive to polarizations and the anisotropy is the same as in the fundamental gap. This high-energy transition is noticeably red-shifted (by $\sim 80$ meV for $E \perp c$ and $\sim 60$ meV for $E \parallel c$) as compared to the value observed at low temperature $E_4^{\parallel,\perp} \sim 1.24 \pm 0.005$ eV, suggesting fundamentally different in nature. Since the CBs above $H_6^{CB}$ and VBs below $H_6^{VB}$ at the H-point are far apart, the next higher energy transition at the H-point beyond $E_3^{\parallel,\perp}$ is not accessible with our
probe beam. Therefore, we attribute the transitions $E^\parallel$ and $E^\perp$ are caused by a direct transition at the L-point. Detailed understanding of higher energy transitions in Te requires further theoretical calculations.

Supplementary Figure 1. Polarized transient reflectance response of Te nanosheets around the band-edge region. a Two-dimensional false color map of pump-probe delay dependent transient reflectance spectra $[\Delta R/R_0(E, t)]$ over an extended probe energies for parallel $E \parallel c$ and perpendicular $E \perp c$ relative to the c-axis of Te crystal. Narrow region of probe energies between 0.72 − 0.8 eV is missing due to technical limitations. Negative signal (red) indicates a pump-induced increase in absorption and positive signal (blue) corresponds to decrease in absorption. Overall, strong features with distinctive dynamics at different energies are clearly visible, suggesting a series of optical transition with some polarization anisotropy. b Transient spectra (blue spheres) acquired at 50 ps time delay with two orthogonal probe polarizations. Each spectrum is fitted with a simple model described in the main text (red dashed lines). Calculated moduli $\Delta \rho_j$ of each fit are also plotted with vertical offset (black lines). Both the model fits and the moduli show transient features corresponding to the series of direct and indirect interband transitions in Te, as indicated by vertical dashed lines. The transition energy for $E \parallel c$ is blue-shifted by $\sim 20$ meV, suggesting band-edge optical anisotropy in Te at room temperature.

B. Carrier dynamics

Polarization dependent carrier decay processes are investigated by measuring TR time traces at different probe energies following excitation of the sample with 1.51 eV pump pulses. Representative polarized
time traces taken from the nanoflake at 300 K from two low- and high-energy regimes are shown in Supplementary Figure 2a,b. At energies intermediate between these two regimes, the TR response is very weak and fast due to lack of any direct optical transitions and, therefore we will not discuss it here. Near the band gap region (Supplementary Figure 2a), the majority of the TR decays exponentially within first 30 ps followed by a very weak (nearly 2-orders of magnitude lower than the peak) residual signal, which persists over 300 ps. Around the high-energy regime (Supplementary Figure 2b), the time traces display initial ultrafast decay of the signal followed by a long exponential recovery of the remaining signal at later times. In order to quantify the overall decay behavior around the low- and high-energy regimes, each time trace is fitted using multi-exponential function, as described in Eq. (2) in the main text. A least square fitting to Eq. (2), as shown by dashed red lines in Supplementary Figure 2a,b estimates the decay time constants $\tau_i$ of each $i^{th}$ decay channel at different bands. Near the low-energy region, the decay constant of the majority of the signal is $\tau_{1}^{\perp} \sim 17 \pm 1$ ps for $E \perp c$ and $\tau_{1}^{\|} \sim 22 \pm 1$ ps for $E \parallel c$, respectively, followed by long-lived ($\tau_{2}^{\perp}$, $\tau_{2}^{\|} \gtrsim 500$ ps) residual signal. Around the high-energy region, only a fraction of the peak intensity decays abruptly within a few ps ($\tau_{1}^{\perp} \sim 10 \pm 1$ ps for $E \perp c$ and $\tau_{1}^{\|} \sim 12 \pm 1$ ps for $E \parallel c$) and the remaining signal decays rather slowly ($\tau_{2}^{\perp}$, $\tau_{2}^{\|} \gtrsim 300$ ps) for both polarizations. The fractional signal of rapid decay is $\sim 50\%$ of the peak signal for $E \perp c$ while it is only $\sim 10\%$ of the peak signal for $E \parallel c$. Such differences of decay dynamics with respect to the polarization and energy of the probe laser beam are qualitatively similar as observed at low temperature (see main text).

Around the low-energy region, ultrafast carrier thermalization by carrier-carrier and carrier-phonon scattering processes is not distinguishable at room temperature. Therefore, the decay time constants of $\tau_{1}^{\perp}$ and $\tau_{1}^{\|}$ for both polarizations are attributed to the interband carrier recombination time including carrier thermalization around the fundamental gap. Due to ultrathin samples, thinner than the typical laser penetration depth $l_{IR}$ in Te around the IR-region ($l_{IR} \sim 50$ nm),\textsuperscript{5} carrier diffusion does not play a role in the decay dynamics. The subsequent weak residual signal (less than a 5% of the peak) observed after the recombination is attributed to a constant feeding of carriers from higher lying bands through phonon-assisted intervalley processes. Around the high-energy region, the carrier decay dynamics is largely associated with the direct transition near the band-edge at the L-point and, therefore, involves fundamentally different scattering processes. The polarized TR responses display sharp transient within $\sim 10$ ps, which is attributed to intervalley scattering followed by the intraband cooling of carriers via carrier-carrier and carrier-phonon scattering. Since the signal after initial rapid decay is reduced substantially with $E \perp c$ as compared to the signal with $E \parallel c$, this observation suggests intervalley
scattering is effectively suppressed with \( E \parallel c \). Subsequent slower decay of the signal is caused by persistent feeding of intervalley scattered carriers at neighboring valleys as well as carriers at higher lying bands to the H-valley. Note that the initial rapid recombination time at all spectral regions is noticeably slower with \( E \parallel c \) as compared to the times with \( E \perp c \). This behavior is more apparent at low temperature (see main text), which is consistent with anisotropic carrier scattering times and hole mobility observed in Te crystal.\(^6\) Overall, carrier decay dynamics at room temperature is qualitatively similar to the low-temperature dynamics, which has been described with sufficient detail in the main text.

Supplementary Figure 2. Polarized transient reflectance response of Te nanosheets at room temperature. Representative polarization resolved transient reflectance (TR) \( \Delta R/R_0 \) traces of Te samples around the fundamental band-edge a and high-energy transition region b. Dashed red lines are the multi-exponential fits of each corresponding data over a long delay range. Around the band-edge region, majority of the TR signal relaxes within first 30 ps due to ultrafast intraband thermalization followed by interband recombination. Around the higher energy transition, about half of the peak TR signal decays rapidly (\( \tau_1 \parallel \sim 10 \) ps) with \( E \perp c \) due to intervalley scattering accompanied by intraband thermalization. In contrast, TR signal with \( E \parallel c \) decays only marginally (10 % of the peak) with a decay constant of \( \tau_1 \parallel \sim 12 \) ps, suggesting suppressed intervalley scattering and weak coupling to phonon. Rest of the signal for both polarizations decay rather slowly (\( \tau_2, \tau_2 \parallel \gtrsim 300 \) ps) due to constant feeding of carriers from higher lying bands to the H-valley.
Supplementary Note 2: Modeling transient reflectance spectroscopy (TRS) data

For simplicity, our model of the transient reflectance response of Tellurium is based on the dominant contribution of band-filling due to interband photoexcitation of carriers. We constrain our calculations by considering the dynamics near the fundamental gap at H-point of bulk Brillouin zone of Te. The photoinduced band filling effect alters the dielectric response of Te, \( i.e., \) a fractional change in the complex refractive index (\( n = n + ik \)), and causes a change in absorption and reflectance of the samples.

Since the imaginary component of the complex refractive index, \( i.e., k \), relates to the absorption coefficient \( \alpha \) as: \( k = \frac{\lambda}{4\pi} \cdot \alpha \), we first begin the model by calculating the photoinduced change in the absorption coefficient \( \Delta \alpha \). The absorption coefficient \( \alpha \) of semiconductors with parabolic bands can be described by the following expression:10, 11

\[
\alpha(E, N_h, N_e, T) = \frac{C_\alpha}{E} \int_0^{E-E_g} \rho_c(E') \cdot \rho_v(E' - E) \cdot \left[ f_h(E - E_g - E', N_h, T) - f_e(E', N_e, T) \right] dE'
\]  

(1)

Where \( \rho_c \) and \( \rho_v \) denote density of states for the conduction and valence bands, \( N_h \) and \( N_e \) are the respective carrier densities for holes and electrons, \( f_h \) and \( f_e \) are the appropriate Fermi-Dirac distributions, \( T \) is the carrier temperature, and \( C_\alpha \) is a constant factor fit to the data. Given the p-doped nature of our samples, we consider the total hole population \( N_h \) as a sum of doped holes \( N_d \) and photoexcited holes \( \Delta N_h \), \( i.e., N_h = N_d + \Delta N_h \). The electron population \( N_e \) is taken to be entirely photoexcited, \( i.e., N_e = \Delta N_e \), and the photoexcited electron and hole densities are taken to be equal, \( i.e., \Delta N_e = \Delta N_h \), on the basis of charge neutrality. The carrier temperature \( T \) is assumed to be equal for electron and holes. Now we calculate the photoinduced absorption coefficient \( \Delta \alpha \) using relevant parameters, which are known for our samples (see Supplementary Table 1).

Once the photoinduced modulation in the absorption is calculated, we can derive the modulation of the real part of index of refraction, \( \Delta n \), using the Kramers-Kronig relation:

\[
\Delta n(E, N_h, N_e, T) = \frac{hc}{\pi} \int_0^{\infty} \frac{\Delta \alpha(E', N_h, N_e, T)}{(E')^2 - E^2} dE'
\]  

(2)

where \( \Delta \alpha \) is calculated from Eq. (1). Note that although the upper bound of the integral is infinite, \( \Delta \alpha \) rapidly approaches zero above the band-edge and thus our theoretical description of the absorption need not include the high-energy regime.
Once we derive both the real part of refractive index and the absorption coefficient, we can connect to these parameters to evaluate the reflectance of the sample. Assuming normal incidence of the probe beam on the sample, which is the case in our experiment, the reflectance of the sample without excitation is given by:

\[ R = \frac{(n - 1)^2 + k^2}{(n - 1)^2 - k^2} \]  \hspace{1cm} (3)

The fractional change of reflectance induced by pump excitation (normalized by initial reflectance \( R_0 \) before exciting the sample) can be expressed (in first-order expansion) as following:

\[
\frac{\Delta R}{R_0} \cong \left[ \frac{8n_o k_o}{((n_o + 1)^2 + k_o^2)^2} \cdot \Delta k(E, N_h, N_e, T) \right] - \left[ \frac{4(1 + k_o^2 - n_o^2)}{((n_o + 1)^2 + k_o^2)^2} \cdot \Delta n(E, N_h, N_e, T) \right]
\]  \hspace{1cm} (4)

Where \( n_0 \) and \( k_0 \) are the background values of the real and imaginary components of the complex index of refraction, respectively. We take \( n_0 \), for light polarized perpendicular to the c-axis, to be constant at the average value of 4.95 for our probe tuning range, based on measurements of single-crystal Tellurium.\(^{12}\)

We calculate \( k_0 = \frac{\lambda}{4\pi} \cdot \alpha \) from Eq. (1) using background estimates for carrier density. All basic material parameters are tabulated in Supplementary Table 1.

We fit theoretical lineshapes from Eq. (4) to our experimental transient reflectance spectra by parameterizing the density of doped holes, density of photoexcited carriers, carrier temperature, bandgap energy, and an overall scaling factor. We numerically optimize these parameters to minimize the sum squared error for each spectrum taken at distinct delay times, keeping the time-independent parameters consistent. The resulting fit parameters are tabulated in Supplementary Table 2.

**Supplementary Table 1: Basic material parameters of Te used for modeling.**

| Parameters               | Values     |
|--------------------------|------------|
| Electron effective mass\(^*\), \( m_e \)\(^4\) | 0.091 m\(_e\) |
| Hole effective mass\(^*\), \( m_h \)\(^4\)      | 0.137 m\(_e\) |
| Refractive index, \( n_0 \)\(^12\)             | 4.95       |

\(^*\)Geometric mean accounting for anisotropy.
**Supplementary Table 2: Band parameters of Te extracted from model fittings of delay dependent TR spectra.**

| Parameters                              | @ 10 ps delay | @ 30 ps delay | @ 60 ps delay |
|-----------------------------------------|---------------|---------------|---------------|
| Carrier temperature, $T_e$              | 84 K          | 67 K          | 47 K          |
| Photoexcited carrier density, $\Delta N_{eh}$ | $1.0 \times 10^{18}$ cm$^{-3}$ | $5.2 \times 10^{17}$ cm$^{-3}$ | $2.9 \times 10^{17}$ cm$^{-3}$ |
| Quasi-Fermi Energy (holes), $E_{fh}$    | 0.031 eV      | 0.027 eV      | 0.026 meV     |
| Fundamental band gap, $E_g$             | 0.319 eV      | 0.319 eV      | 0.319 eV      |
| Doping Density, $N_d$                   | $1.8 \times 10^{18}$ cm$^{-3}$ | $1.8 \times 10^{18}$ cm$^{-3}$ | $1.8 \times 10^{18}$ cm$^{-3}$ |

**Supplementary Note 3: Polarization anisotropy of optical reflectance in Te**

The ground-state optical transitions can be studied by measuring the linear optical absorption or reflectance of the samples. Such measurements are sometimes quite challenging in substrate (high absorbing substrates) supported ultrathin samples due to dominant contributions from the substrate. Linear dichroism, *i.e.*, polarization anisotropy of optical absorption or reflectance, otherwise, can be very useful to reduce the substrate contributions and enhance the sensitivity of detecting optical response of the sample, particularly in anisotropic crystals. Here, we demonstrate that it is indeed possible to observe band-edge absorption features in a typical reflectance measurement of Te nanosheet samples supported on ∼ 350 nm SiO$_2$ grown Si substrate. We observe the response of clearly distinguishable ground-state optical transitions, which are otherwise hardly visible from the reflectance spectra of the sample with substrate.

**Supplementary Figure 3** displays probe photon energy dependent optical reflectance anisotropy (RA) of Te nanosheets measured at 10 K. The RA is deduced by measuring the difference in reflectance for light normally incident and linearly polarized along two orthogonal directions, *i.e.*, parallel $E \parallel c$ and perpendicular $E \perp c$ to the c-axis of the Te crystal. The normalized RA is expressed by: $RA = (R_\parallel - R_\perp)/(R_\parallel + R_\perp)$, where $R_\parallel$ and $R_\perp$ denote the reflectance along $E \parallel c$ and $E \perp c$, respectively. The individual reflectance spectra of each polarization are also shown in the inset. The anisotropy is particularly pronounced around the band-edge regions, which are shown by thick grey lines and also indicated by particular transitions in the band structure. The first minimum coincides
with the $H_4 \rightarrow H_6^{CB}$ transition between the uppermost $H_4$ VB to the lowermost $H_6$ CBs, \textit{i.e.}, $E_1 = E_1^\perp$ and $E_1^{\parallel}$. The next maximum matches with the $H_5 \rightarrow H_6^{CB}$ transition between the spin-split lower $H_5$ VB to the $H_6$ CBs, \textit{i.e.}, $E_2 = E_2^\parallel$. The positive peak of the RA is due to 180° phase shift of this transition, which is dipole forbidden for $E \perp c$. Weak maxima around the other two higher energy transitions $E_3 = E_3^{\perp,\parallel}$ and $E_4 = E_4^{\perp,\parallel}$ can also be recognized in the spectra. Overall, these RA features are consistent with the features observed in transient reflectance spectra and further supports our estimations of ground-state optical transitions in our Te samples.

![Supplementary Figure 3](image)

**Supplementary Figure 3. Polarization anisotropy near the band-edge of Te nanosheets.** The polarization anisotropy is calculated from the reflectance spectra (shown in the inset) recorded for both $E \perp c$ and $E \parallel c$ polarizations with respect to the c-axis of the Te crystal. The anisotropy peaks near the band-edges of different bands around H-point of the Brillouin zone. Respective transition energies are also indicated with transparent grey thick lines. These transition energies are consistent with ground-state transitions extracted from the TR spectra (see main text).
**Supplementary Note 4: Coherent longitudinal acoustic phonon in Te nanosheets**

Coherent longitudinal acoustic phonons (CLAP) are propagating ultrasonic strain waves in solid crystals, which can be excited efficiently at the surface by ultrafast laser pulses through transient lattice deformation.\textsuperscript{13-16} Since the strain wave propagation modifies the local dielectric properties of the materials, the induced oscillatory behavior of dielectric properties can be probed in the time-domain by various pump-probe spectroscopic techniques.\textsuperscript{13, 17}

**Supplementary Figure 4** displays probe wavelength dependent transient reflectance signal (TRS) data measured following 1.51 eV pump excitation of the Te nanosheet samples and probing at different photon energies (wavelengths). Following initial ultrafast transients, the TRS signal oscillates in time and gradually decays because of interference between light waves reflected off the surface and light waves reflected off the propagating strain wave. The TR signal therefore contains both the electronic response of the material as well as the oscillatory interference signal due to the CLAP generated in the sample. In order to extract information about the oscillatory signal, each trace is fitted with following empirical function:

\[
\frac{\Delta R}{R_0}(t) = A + \left( B \cdot e^{-\frac{t}{\tau_1}} \right) + \left( C \cdot e^{-\frac{t}{\tau_2}} \right) + \left\{ D \cdot \cos \left( \frac{2\pi t}{T} + \varphi \right) \cdot e^{-\frac{t}{\tau_{osc}}} \right\},
\]

where first three terms fit the non-oscillatory electronic response including bi-exponential (initial fast $\tau_1$ followed by slower $\tau_2$) response and last one fits the slowly decaying oscillatory signal. Coefficients $B, C, D$ are amplitude of each decaying components and $A$ is the overall background signal. Least square fitting method is applied to each wavelength dependent trace, as shown by black line superimposed on each trace, and useful parameters such as the velocity of the CLAP are extracted as fit parameters. An average amplitude of the oscillation is of the order of $10^{-4}$ and damping constant $\tau_{osc}$ varies from 50-100 ps. Interestingly, the oscillation period $D$ remains unchanged for each probe wavelength. This behavior suggests that standing wave condition of CLAP propagation within the film is fulfilled, which is expected in ultrathin samples. The period of the oscillation is determined by film thickness $d$:

\[
T = \frac{2 \cdot d}{v_S},
\]

where $v_S$ is the velocity of CLAP (sound velocity), which depends on the polarization of probing laser pulse. An average oscillation period of $26.3 \pm 0.1$ ps estimates the average velocity $v_0$ of the LA phonon (sound velocity) of $\sim 1800$ m/s in our ultrathin ($d \sim 24$ nm) Te samples. The estimated velocity $v_0$ is lower than both the sound velocity along parallel (i.e., 3400 m/s) and perpendicular to the c-axis (i.e.,
2290 m/s), but higher than the velocity along $xy$-plane (shear plane), i.e., (i.e., 1390 m/s), suggesting quasi-shear wave propagation in our sample.\textsuperscript{18}

It is important to discuss the physical origin of the acoustic phonon generation in our Te samples. There are mainly three possible mechanism of stress generation upon photoexcitation: (1) thermoelastic stress ($\sigma_{TH}$), (2) electron-acoustic deformation potential stress, $\sigma_{DP}$ and (3) inverse piezoelectric stress, $\sigma_{IP}$.

The photoinduced $\sigma_{TH}$ due to rapid lattice heating by electron-phonon coupling can be estimated by following the standard model.\textsuperscript{14} $\sigma_{TH} = -3 \cdot \beta \cdot B \cdot \Delta T$, where $\beta$ is the linear thermal expansion coefficient, $B$ is the bulk modulus and $\Delta T$ is the maximum temperature increased by pump pulse. Due to the anisotropic crystal, Te has negative expansion coefficient parallel to c-axis, i.e., $\beta = -5 \times 10^{-6}$ K$^{-1}$, and positive coefficient perpendicular to c-axis, i.e., $\beta = 5 \times 10^{-6}$ K$^{-1}$. The bulk modulus in Te is $B = 19 \text{ GPa}$.\textsuperscript{20} It is known that electron temperature immediately after pump excitation of Te sample is extremely high due to excitation of hot carriers, which thermalizes to the lattice temperature within a ps through electron-optic-phonon coupling.\textsuperscript{21} The lattice temperature increases at most only few K given the low excitation density used in our low-temperature (10 K) experiment. Therefore, we can safely assume an upper bound increased lattice temperature of $\Delta T = 20 \text{ K}$ within 10 ps. Now, using all these parameters the photoinduced thermoelastic stress $\sigma_{TH}$ can be estimated to be $|\sigma_{TH}| \approx 0.006 \text{ GPa}$, which will be even smaller at later delay times. Next, the electron-acoustic deformation potential stress $\sigma_{DP}$ can be estimated by:\textsuperscript{14} $\sigma_{DP} = -a_{e-ac} \cdot \Delta N \approx -0.0003 \text{ GPa}$, with $a_{e-ac} = -8.5 \text{ eV}$ along c-axis\textsuperscript{22} and with photoinduced carrier density of $\Delta N \sim 2 \times 10^{23} \text{ m}^{-3}$. The stress perpendicular to c-axis increases to $\sigma_{DP} \approx 0.001 \text{ GPa}$, with $a_{e-ac} = 35 \text{ eV}$.\textsuperscript{22} If we estimate the band gap change from these stress values,\textsuperscript{23} these stress values are too small to induce tens of meV band gap shifts that we observed in our samples. Therefore, we argue that the piezoelectric strain induced by inverse piezoelectric effect (IPE) is the most likely mechanism of strain generation in our samples. Based on experimental observations, piezoelectric shear strain is dominant in our samples. With simple theoretical expression,\textsuperscript{24, 25} $\Delta E_{sp} \approx 4 \cdot \Psi_{d} \cdot \mathcal{E}_{xy}$, where $\Delta E_{sp}$ is the band splitting, $\Psi_{d}$ is the shear deformation potential and $\mathcal{E}_{xy}$ is the shear strain, it is possible to estimate the shear strain value of the materials if we know the shear deformation potential and the resulting strain induced band splitting. Since we know the band splitting of $\Delta E_{sp} \sim 20 \text{ meV}$ from the TRS experiment at low temperature and the acoustic shear deformation potential of $\Psi_{d} \sim 5 \text{ eV}$ (assuming that the shift of energy gap in Te with dilation),\textsuperscript{26} the shear strain turns out to be on the order of $10^{-3}$. Despite our simple estimation of photoinduced strain in our Te samples, which is an order of smaller than the value estimated
by theory\textsuperscript{27} for $H_6^{CP}$ band splitting, it is plausible to consider photoexcitation as an alternative and non-destructive means for inducing exotic topological phases in Te.

Supplementary Figure 4. Coherent longitudinal acoustic phonon in Te nanosheets. Transient reflectance signal (TRS) of Te samples measured at different probe energies following 820 nm pump excitation at room temperature. Probe beam is polarized off-axis to $ab$-plane as well as $c$-axis but fixed for each wavelength. The TRS traces display weak oscillations embedded on a slowly decaying electronic signal. The oscillatory signal is caused by interference between the probe laser beam and photoinduced strain pulse propagation in the sample. Due to ultrathin samples, standing wave condition is fulfilled, which satisfy the linear dependence of oscillation period with film thickness, but does not depend on wavelength of the probe beam (see inset). This condition allows to estimate thickness knowing the acoustic wave velocity or vice versa through: $T = 2 \cdot d / \nu$, where $d$ is sample thickness, $T$ is the oscillation period, $\nu$ is the velocity of longitudinal acoustic phonon, \textit{i.e.,} sound velocity, in Te. An average period of the oscillations is estimated to be 26.33 ps, which estimates the sound velocity of $\sim 1800 \text{ m/s}$ in our 24 nm thick Te samples.
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