Supporting Information:
Measuring Photoexcited Electron and Hole Dynamics in ZnTe and Modeling Excited State Core-Valence Effects in Transient Extreme Ultraviolet Reflection Spectroscopy

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S1. Dopant characterization of intrinsic bulk ZnTe

To rule out the possibility of mid-gap defect states that could potentially lead to the experimentally observed transient decrease in reflectivity within the gap, we perform X-ray photoemission spectroscopy (XPS) and a 4-point probe measurement on intrinsic bulk ZnTe.

Figure S1 shows an XPS survey on bulk ZnTe. While carbon and oxygen on the surface are observed, there is no evidence for hetero-atom dopants. Quantification furthers shows a
roughly 50:50 Zn:Te ratio. Figure S2 shows the 4-point probe measurements. The resistivity is measured to be \( \rho = (1.26 \pm 0.3) \times 10^9 \Omega \text{cm} \). The dopant density \( n \) is related to the resistivity via \( \rho = \frac{1}{e\mu n} \), where \( \mu \) is carrier mobility and is estimated to be \( \mu \approx 100 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \). The dopant density is estimated at \( 5 \times 10^7 \text{cm}^{-3} \). The dopant density is too small to be responsible for the observed mid-gap transient spectral feature, whose amplitude is comparable to the transient reflectivity change caused by high concentrations of photoexcited carriers at \( 10^{20} \text{cm}^{-3} \).

Figure S1. XPS measurements on intrinsic bulk ZnTe. Carbon and oxygen are observed on the surface. No hetero-atom dopants are observed.
S2. Growth and structural characterization of sputter-deposited ZnTe thin films

ZnTe thin films were prepared on a 50.8 mm x 50.8 mm Corning EXG glass substrate by RF sputtering from a ZnTe target. A stainless-steel 130 μm thick shadow mask was placed over the substrate to create two distinct regions: a large blanket film and smaller discrete patterns. The substrate + mask assembly was clamped to an Inconel plate which was heated by a SiC serpentine resistance heater. The plate was held at the setpoint of 300 °C for a minimum of 1 hour prior to deposition. Chamber pressure at this temperature was 3 x 10⁻⁷ Torr prior to flowing any process gases. During the sputter process, 16 sccm of Ar was flowed through the system and the pumping was throttled to achieve the desired growth process pressure of 2.7 mTorr. The plate was rotated at approximately 30 revolutions per minute during the 2-hour growth. Samples were cooled under Ar prior to being removed from the growth chamber.

The blanket region of the ZnTe film was characterized by X-ray diffraction (XRD) at 22 distinct points (Figure S3) to verify structural uniformity as a function of position. XRD patterns were collected by a 2D solid state detector scanning in an ω-2θ geometry using Cu-Kα radiation. Figure S4 shows the resulting XRD patterns for all 22 points as a false color plot. No appreciable
changes were observed in diffraction patterns between points. An intensity vs. $\theta$ line scan from point 10 is also shown. Comparing the experimentally measured diffraction pattern against a simulated pattern generated using a reference ZnTe crystallographic information file (Inorganic Crystal Structure Database entry #77072), we find that the peak positions match and the ZnTe film adopts the expected zincblende crystal structure. The high relative intensity of the (111) peak at ca. 25° in the experimental data (versus the reference pattern) is attributed to crystallographic texture.

Figure S5 shows film thickness measurements collected from three different regions using a stylus profilometer. The regions were from the masked portions of the film and geometrically equivalent to the positions of points 3, 9, and 17 (Figure S3). Raw profilometry data were notably sloped and bowed. A first-order polynomial subtraction was carried out to flatten the profiles over the region of interest (i.e., the masked ZnTe sample), but higher-order bowing was ignored. As seen in Figure S3, the sampled points are ca. 400-450 nm thick. It is difficult to pinpoint whether any discrepancies between the points are due to nonuniformity or experimental factors, such as substrate topology, shadowing from the stainless-steel mask. 100 nm thick calibration samples grown with nominally identical chamber conditions were measured by X-ray reflectometry (XRR), and thicknesses over a similar area were uniform to ±2 nm with <1 nm RMS roughness.

![Figure S3. Spatial map of point locations on a 25.4 mm by 50.8 mm region of the glass substrate used to verify uniformity of ZnTe thin films.](image)
**Figure S4.** X-ray diffraction from the ZnTe thin films. The false color map shows uniformity of the XRD patterns from the 22 sampled points. A reference pattern (generated from Inorganic Crystal Structure Database entry #77072) and line scan (collected from point 10) presented using more typical intensity vs. 2-theta axes are also provided.
Figure S5: Stylus profilometry collected from ZnTe thin films. Data were collected from a part of the substrate with masked regions, with the points being symmetrically equivalent during growth to those shown in Figure S3.

S3. Ground state optical sample characterization

The band gap of both bulk and thin film ZnTe was determined using UV-VIS spectroscopy (Cary 5000) (Figure S6, S7). The PRISA software was used to calculate the bandgap of the thin film sample while also mitigating thin-film interference effects\(^1\). Figures S6 and S7 present \((\alpha h\nu)^{1/r}\) vs energy plots where \(r = 1/2\) for direct allowed transitions. The estimated direct bandgap is found to be 2.19 eV and 2.18 eV for bulk and thin films, respectively.
Figure S6: Tauc plot of the ZnTe bulk. The direct band gap is measured to be 2.19 eV.

Figure S7: Tauc plot of ZnTe thin film. The direct band gap is measured to be 2.18 eV.

S4. Experimental setup: Transient extreme ultraviolet reflection spectrometer

The reported bulk ZnTe measurements are obtained using photoexcitation of a ~50 fs, 400 nm frequency doubled output of a BBO crystal with p-polarization, pumped with an 800 nm, 1 kHz regeneratively amplified Ti:Sapphire laser (Coherent Legend Elite Duo). The optical excitation fluence is 1.74 mJ/cm², resulting in an initial photoexcited carrier density of $5.41 \times 10^{20}$ cm⁻³. Transient reflection is measured by varying delay times between the excitation and probe pulses using an optomechanical delay stage. The photoexcited carrier dynamics are probed with
an XUV pulse produced by high-harmonic generation in argon with an s-polarized few-cycle white light pulse (<6 fs, 550 nm - 950 nm, Figure S8). The residual white light beam is removed with a 200 nm thick Al filter (Lebow). The generated XUV continuum is used to probe the Te N\textsubscript{4,5} absorption edges around 40 eV. A typical XUV spectrum is shown in Figure S9. An edge-pixel referencing scheme was used to reduce noise due to intensity fluctuations based on signal-free spectral regions.\textsuperscript{2} The reflection measurement uses a 10-degree grazing incidence geometry (80 degrees from normal incidence).

The static sample reflectivity around the Te N\textsubscript{4,5} edge is shown in Figure S10. The reflectivity decreases around the conduction band minimum (around 40 eV from Te 4d core states). The static XUV reflectivity of ZnTe is found by dividing the measured static reflectivity spectrum of ZnTe by the static reflectivity of a Si wafer, which does not have any absorption features in this energy region.

**S4.1. Characterization of few-cycle white light pulse for XUV pulse generation**

A dispersion scan (d-scan, Sphere Ultrafast Photonics)\textsuperscript{3} was used to characterize the broadband white light few-cycle pulse used for XUV pulse generation. In this method, a pair of glass wedges with known dispersion are inserted in the beam path. The second harmonic spectra of the white light generated with a BBO crystal are measured as a function of introduced dispersion through wedge insertion. The electric field of the few-cycle pulse can be retrieved based on the reconstruction algorithm of the d-scan trace.
**Figure S8.** Characterization of few-cycle white light pulse with dispersion scan (d-scan). (a) Measured second harmonic spectra as a function of wedge insertion. (b) Reconstructed d-scan trace. (c) White light spectrum (red line), spectral phase (blue line) and polynomial fit of the spectral phase (black line). (d) Retrieved white light pulse has an intensity profile with a temporal FWHM of 4.9 fs.

**S4.2. Representative XUV probe spectrum**

The XUV probe pulse is produced through high-harmonic generation in an Ar gas cell. Figure S9 shows a representative normalized XUV spectrum reflected from ZnTe with a 10 degree incident angle (80 degrees from normal incidence).
Figure S9. Representative reflected XUV spectrum from ZnTe with a 10 degree incident angle relative to the sample surface (80 degrees from normal incidence). The energy range of the selected spectrum is defined by the physical size and position of the detector to cover the Te N_{4.5} edge.

S5. Theoretical methods: Ground state and excited state core-level spectra

To fully analyze the transient core-level spectra, state blocking, and the associated changes in screening of the core-valence exciton must be considered, as well as any potential change in spin-orbit coupling and angular momentum effects. These changes are calculated using an ab initio combined theoretical approach based on density functional theory (DFT) and the Bethe-Salpeter equation (BSE). The existing OCEAN code$^{4,5}$ (Obtaining Core-level Excitations using Ab-initio calculations and the NIST BSE solver) is modified to accept excited state distributions to determine how the ground state band structure relates to the observed XUV spectra and transient changes. In this procedure, the band structure and the ground state wavefunction are first calculated using DFT (Quantum Espresso)$^6$. The BSE is solved to obtain core-valence exciton wavefunctions including spin-orbit coupling and Coulomb screening of the core-valence exciton. The reflectivity spectra are calculated from the complex dielectric function as calculated by OCEAN and converted using the Fresnel equations.

S5.1. Ground state calculation
XUV reflection spectra were calculated with the OCEAN\textsuperscript{4,5} code based on a converged DFT calculation\textsuperscript{6}. The DFT and BSE calculations are solved using a $20 \times 20 \times 20$ k-point mesh. We use 9 valence bands and 31 conduction bands in our calculation. The DFT calculation uses the norm-conserving generalized gradient approximation (GGA), Perdew-Burke-Enzerhof (PBE) pseudopotentials, a 300 Rydberg energy cut-off, and a converged lattice constant of 6.10 Å. The OCEAN code uses the projector augmented wave method (PAW) to calculate core-level transition matrix elements, which are then used in the BSE equation to calculate final states as modified by the core hole. The OCEAN BSE calculation uses a screening mesh of $4 \times 4 \times 4$, a dielectric constant of 10.4, a 4.0 Bohr screening radius, and a 0.7 scaling factor for the slater G parameter. A post-calculation broadening is used as a fitting method to achieve similar linewidth to that observed in the experiment. The DFT calculation underestimates the band gap of ZnTe. After DFT calculation, we add a band gap correction by scissor shifting conduction bands up by 1.02 eV to achieve a correct band gap. In this theoretical framework, both the real and imaginary dielectric function are directly calculated in the OCEAN code, allowing easy comparison between theory and experiments done in transmission or reflection configurations.

Figure S10 shows the calculation of the ground state complex dielectric function (Figure S10(a)), as well as the calculated reflectivity, overlaid with the experimentally measured static sample reflection around the Te N\textsubscript{4,5} edge (Figure S10(b)). The measured ZnTe XUV reflection is normalized to a Si wafer, which doesn’t exhibit any sharp spectral features around 40 eV. By referencing to Si, the typical high-harmonic intensity profile is removed from the static reflection spectrum. However, the absolute reflectivity of ZnTe and Si is difficult to obtain as variance of sample surface roughness affects XUV reflectivity, such as Debye-Waller factors. For this reason, a normalized reflectivity is shown in Figure S10(b).

As shown in Figure S10, the OCEAN calculation reproduces Te edges. However, it underestimates the pre-edge absorption. In OCEAN, the calculation assumes perfect crystals, where there is no pre-edge absorption. For actual samples used in experiments, many effects can contribute to the pre-edge absorption, including but not limited to an imperfect crystal lattice, surface states, an imperfect bonding environment, and surface-modified lattice configurations. We note that the discrepancy between the calculated and measured ground state reflection plays a much lesser role in the excited states interpretation. The reason is that for the excited states calculation, we compare the changes in transient reflectivity, defined as $\Delta OD = - \log_{10} \left( \frac{I_{\text{pump on}}}{I_{\text{pump off}}} \right)$. 
Under this definition, systematic error such as underestimated pre-edge absorption largely cancels during the normalization between pump on and pump off spectra.

![Figure S10](image)

**Figure S10.** (a) Calculated ground state complex dielectric constant. (b) Calculated ground state reflectivity, overlaid with experiment. Experimentally measured reflection is normalized to a Si wafer to remove the high harmonic profile in the spectra.

### S5.2. Excited state calculation

To capture the photoexcited electrons and holes, we modify the OCEAN package, which allows us to selectively forbid or allow XUV transitions to the conduction or valence bands at different momentum k-points. In this experiment, we aim to understand carrier thermalization from the initial photoexcited states to the band gap minimum at the Γ point. To simulate this charge transfer process, we discretize the states between the initial photoexcited states and the final states across the direct band gap at the Γ point into a combination of 9 different electron configurations in the conduction bands and 9 different hole configurations in the valence band. The discretization is based on the energy difference between conduction and valence bands. As a result, each discretized electron and hole configuration consist of multiple k-points in momentum space. The calculated excited states spectra of the total 81 combined electron and hole configurations is shown in Figure S11. The calculation is performed on a $20 \times 20 \times 20$ mesh in k-space. Under this condition, both electron and hole thermalization can be seen, with electron and hole energy resolution at $\sim 60$ meV (calculated carrier energy difference between neighboring hole configurations). Better resolution
can be further achieved by increasing the k-space sampling rate or interpolating the spectra between adjacent carrier distributions.

The momentum-resolved differential XUV transition probability amplitudes in Fig. 2(b) are calculated by solving the core-valence wavefunctions using the OCEAN generalized minimal residual method (GMRES) solver instead of the Haydock method used for calculations of spectra.

When comparing theory with experiment, it is worth noting that in the excited states calculation, we do not input the actual carrier density (in units of $10^{20}/\text{cm}^3$) in our calculation. Rather, we fully allow or forbid XUV transition to certain states in the conduction or valence bands. For this reason, we do not simulate carrier density evolution as a function of time, which is encoded in spectral intensity and is related to recombination and diffusion. It is the simulated peak position, or peak energy (related to the hot carrier energy), rather than peak amplitude (associated with carrier density) that we use to compare between experiment and theory.

A tentative reconstruction of the transient data is shown in Figure 2(c) of the manuscript, where we fit the calculated excited state spectra to the measured transient spectra at each pump-probe time delay. The reconstruction is performed for the first 800 fs after photoexcitation, before phonon modulation dominates the spectra while the carrier relaxation largely finishes. Initial hot electron and hole thermalization is observed in the theoretical reconstructed transient XUV spectra. While an overall thermalized trend can be reconstructed, in the current example it is difficult to assign the measured transient reflectivity at each pump-probe delay to a unique carrier configuration. The resolution is limited by k-space sampling rate, small excess kinetic energy of carriers from photoexcitation, and spectral fluctuations from the experiment. This method will work best when the hot carriers have large excess kinetic energy compared to the band gap and when the band structure is highly dispersive. In principle, this approach allows the theory to reproduce state filling effects, carrier energy and momentum distributions, and relaxation pathways, which could be of importance in various solar-driven semiconductor processes such as multi-exciton generation.
Figure S11. Calculated excited state XUV differential spectra under different carrier configurations. States between the initial photoexcitation and the final states at the Γ point are discretized into 9 electron energy configurations and 9 holes energy configurations, with a combined total 81 unique electron-hole energy configurations. In this plot, 81 configurations are plotted and sorted by increasing electron and hole energy. For example, the carrier configuration indices (y axis) 1 to 9 corresponds to having holes fixed at the lowest energy states (around the Γ point), while sweeping 9 electron configurations from low energies to high energies. Similarly, the carrier configuration indexes 10 to 18 plot the same 9 electron configurations, but under a different hole configuration with a higher hole energy. Clear electron and hole thermalization can be seen in this plot.

S6. Transient XUV spectra on ZnTe thin films and under different pump intensities

The many-body nature of the mid-gap transient spectral feature reported in Figure 1 is further confirmed by performing a transient XUV reflection measurement on high quality ZnTe thin films (sample characterization in Supplementary Information section S2). The transient XUV reflection spectra are shown in Figure S12. In Figure S12(a), a similar mid-gap transient spectral signature is observed, as compared to the bulk ZnTe measurement reported in the main text. This measurement rules out the possibility of the mid-gap response being dependent on the method of sample growth, and strongly suggests that it is an intrinsic response of ZnTe, regardless of sample
growth methods. We further conclude that the mid-gap response depends on the photoexcited carrier density. Figure S12(b) shows the transient XUV reflection measured at a higher excitation density of 1.59 mJ/cm². Under higher carrier density, the mid-gap dynamics are more pronounced, where both the redshift and the lifetime are increased. This is consistent with the assignment of many-body driven band gap renormalization, where higher carrier densities will increase energy shifts as well as increase the lifetime as it takes longer for more carriers to reach equilibrium.

In addition to enhanced band gap dynamics, at higher excitation intensity we also observe strong spectral intensity oscillations (Figure S12(b)). Fourier transformation between 40.2 eV and 41.4 eV reveals oscillation peaked at 2.79 THz (Figure S13). This frequency is associated with acoustic phonon branches with wave vectors between Γ-K and Γ-L regions.

**Figure S12.** Transient XUV spectra of ZnTe thin film. (a) Similar transient XUV signature compared to bulk measurements in Figure 1 are reproduced on the thin film sample with an excitation density of 1.06 mJ/cm², suggesting the mid-gap feature is intrinsic to ZnTe and does not depend on the sample growth method. (b) At a higher excitation intensity of 1.59 mJ/cm², both the spectral redshift and the lifetime of the band gap dynamics are increased. This observation is consistent with the assignment of the many-body induced band gap renormalization picture to the measured in-gap dynamics. Spectral intensity oscillations potentially due to acoustic phonons are also observed.
Figure S13. Frequency spectrum of intensity oscillations between 40.2 eV and 41.4 eV of the data shown in Figure S12(b) reveals an oscillation frequency of 2.79 THz. This frequency is associated with acoustic phonon branches with wave vectors between Γ-K and Γ-L regions.

S7. Nanosecond transient XUV measurement
As a complementary measurement to the fast femtosecond-to-picosecond carrier relaxation dynamics presented in the manuscript, here we report the measurement of transient XUV spectra up to 1 ns (Figure S14). The scanned time points are sampled on a logarithmic scale, and the pump-probe temporal overlap has an offset of 2 ps, as shown in Figure S14. The spectral intensity of the electronic Te 4d_{5/2} to conduction band transition around 40 eV only exists for the first ~ 10 ps and is quickly replaced with the overlapped Te 4d_{3/2} to valence band transition (hole signature). For this reason, we use the intensity of 4d_{3/2} to conduction band transition to track the hot carrier lifetime. Unlike the electron and hole diffusion rates of 2.21 ± 1.12 ps and 3.91 ± 3.58 ps reported in the manuscript, we do not observe any significant signal decay at longer timescales up to 1 ns. This suggests that the signal intensity drop reported in Figure 3 is likely due to surface carrier diffusion, while the intrinsic carrier lifetime is significantly longer than 1 ns.
Figure S14. Transient XUV reflection measurement to 1 ns. No significant carrier recombination is observed, suggesting that the intrinsic carrier lifetime is longer than 1 ns.

References