Supporting Information for “Snapshots of Dirac fermions near the Dirac point in topological insulators”

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S1. Sample preparation

Sample #1: This was grown by the vertical Bridgman method. Preliminary homogenization was carried out in a horizontal tube furnace at 350 °C for 75 h. The sealed ampoules were then passed through a vertical Bridgman furnace between 650 and 600 °C of thermal gradient ~1 °C/cm near the solidification point. The pulling rate was kept at 0.2 mm/h to maintain the slow-cooling process from 850 °C to 650 °C at a rate of 2 °C/h and then quenched in cold water.

Sample #2 & #4: These were grown by a modified floating zone method, where the Se-rich Bi_2Se_3 was used in the melting zone. The Bi_2Se_3 material, of high-purity (99.9999%) Bi and Se, was premelted and loaded into a 10-mm diameter quartz tube. The crystal growth rate was controlled at 0.5 mm per hour.

Sample #3: The charge prepared from elementary Bi (5N) and Se (4N) in composition $\text{Bi}_2\text{Se}_{3.01}$ was sealed into the fused quartz ampule evacuated up to $\sim 10^{-4}$ Torr. High-purity bismuth was prepared in NIIC (Novosibirsk, Russia). The mixture heated up to 20 °C above the melting temperature was kept for 24 h to complete the reaction between the components, and then it was cooled together with the furnace. The synthesized polycrystalline ingot was reloaded into the special quartz ampule with a conical tip for recrystallization by a modified vertical Bridgman method using the rotating heat field. To prevent sticking between the growing crystal and fused quartz, the internal walls of the ampule were coated with pyrolytic carbon. The ampoule translation rate and axial temperature gradient were 10 mm/day and ~ 15 °C/cm, respectively. As a result, a crystal 9 mm in diameter and 60 mm long was obtained.

All samples were kept in a vacuum tank to avoid surface oxidation. Before optical measurements, scotch tape was used to cleave the (001) surface of the Bi_2Se_3 crystals, ensuring a flat and bright surface to degrade the oxidation for optical measurements¹. The TI surface state of the perfectly cleaved (0001) surface of the bulk topological insulator stays intact during a long-term storage in the atmosphere. The carrier concentrations (n) of all samples were obtained by Hall measurements as listed in Table I.

S2. Experimental setup of optical pump mid-infrared probe

Figure S1 shows the setup of the optical pump mid-infrared probe (OPMP) spectroscopy. The light source was provided by the regenerative amplifier (Legend, Coherent Inc.) operating at a central wavelength of 800 nm with a repetition rate of 5 kHz, a spectral width of 35 nm and a pulse duration of 30 fs. A beam splitter reflected 40% of light into the pump path, whereas the remnant was transmitted and served as a probe. In the probe path, a 0.7-mm-thick GaSe crystal was used to generate mid-infrared pulses with the tunable wavelengths from 8.1 (153 meV) to

14.3 μm (87 meV) via the differential frequency generation (DFG).

To ensure the spot size of pump beam is larger than that of the probe beam, the optical pump beam was focused on the sample with a diameter of 500 μm via 150-mm lens. Additionally, the pumping fluence used in this study was lower than 150 $\mu\text{J}/\text{cm}^2$ to prevent damage to the samples. The mid-infrared probe beam was focused on the sample surface with a diameter of 500 μm through an $f = 200$ mm Au coated off-axis parabolic mirror. This beam was collimated and refocused onto a liquid-nitrogen cooled HgCdTe detector by an $f = 50$ mm Au coated parabolic mirror. The incident angles of optical pump and mid-IR probe beams are $\sim 33^\circ$ and $\sim 15^\circ$, respectively.

S3. Characterization of tunable mid-infrared pulses

The spectra of the generated pulses are characterized using an interferometric correlation technique demonstrated in Ref. [2]. The center wavelength of the mid-infrared pulses was continuously tuned by rotating the GaSe crystals which varied the phase-matching angles in GaSe crystals. Fig. S2a shows the spectra obtained in the phase-matched configuration for different phase-matching angles. The spectra exhibit a bandwidth of 4 meV. The corresponding wavelengths, 8.1 μm (153 meV) to 14.3 μm (87 meV), and the pulse energies are given in Fig. S2b. Finally, the spectral resolution of our OPMP system is around 4 meV.

S4. Temporal resolution

The temporal resolution in our OPMP spectroscopy was determined by the result of Ge, as shown in Fig. S3a. The rise time (~ 1 ps) of transient reflectivity change ($\Delta R/R$) in Ge is much longer than that in typical semiconductors (~ 300 fs)³. This unusually long rise time is due to the limit of temporal resolution in our OPMP system. Thus, the differentiated result of the fitting curve gives a temporal resolution of about 500 fs (Fig. S3b).

S5. Determining the penetration depth of 800 nm

The penetration depth in the optical range was determined using the static reflectivity measurement. We measured the reflectivities for s- and p-polarizations (R_s , R_p) with various angles of incidence (Fig. S4). The experimental data were fitted using the complex Fresnel equations. From the results of fitting, we obtained the complex refractive index of our samples. The real part ($Re[n]$) is about 5.5 and the imaginary part ($Im[n]$) is about 2.7. Moreover, the latter gives a penetration depth of 23.5 nm, which is similar to the values of previous studies^{4,5}.

S6. Angle resolved photoemission spectroscopy and determining the carrier concentration of surface and bulk states

The carrier concentration of surface state n_{surface} listed in Table I was estimated from Angle-Resolved Photoemission Spectroscopy (ARPES) band dispersion image. ARPES was carried out at BL21B1 beamline NSRRC, Taiwan. Samples were *in-situ* cleaved in the base pressure of 4.9×10^{-11} Torr. All spectra were taken at 13 K with photon energy of 22 eV. Overall energy resolution is better than 8 meV. Additionally, the amount of surface electron density can be estimated from the occupied area of Fermi surface (FS) on the whole Brillouin zone (BZ)⁶. Therefore, the number of electrons per surface unit cell (UC) is the occupied area of the 2D FS mapping/the area of surface BZ without counting the spin degeneracy. The electron concentration of surface state n_{surface} can be estimated by the following equation⁶

$$n_{\text{surface}} = \frac{A_{\text{FS}}}{A_{\text{BZ}} A_{\text{UC}}} = \frac{\pi K_F^2}{(4\pi^2/a^2)(a^2)} = \frac{K_F^2}{4\pi} \quad (\text{S1})$$

where K_F is the Fermi wave number which can be obtained from the ARPES band dispersion image, A_{FS} is the area of Fermi surface, A_{BZ} is the area of Brillouin zone, and A_{UC} is the area of unit cell. Moreover, the n_{surface} is also dependent on the Fermi level E_F , which is as a function of K_F . Namely, the n_{surface} increases while the bulk carrier concentration (n_{bulk}) rises. The bulk carrier concentrations n_{bulk} were obtained by using the Hall measurements and listed in Table I.

S7. Reflectance spectra and penetration depth in mid-IR

Figure S5 shows the reflectance spectra (solid lines) of all Bi_2Se_3 used in this study. By fitting with Drude model (using *RefFIT* program), the imaginary part of refractive index can be obtained. Then the photon energy-dependent penetration depth δ can be further calculated by $1/\delta = 2\omega k/c$ (ω is the angular frequency of 800-nm pump beam, $k=2.7$ is the imaginary part of refractive index which is obtained from Fig. S4) as shown in Fig. S6. The penetration depth increases while the carrier concentration decreases.

The penetration depth of 800-nm pump and mid-IR probe are ~ 24 nm and 300 nm ~ 1 mm, respectively, which is much larger than the penetration depth of ~ 1 nm in ARPES experiments. Due to the sufficient detection depth and the saturation of surface changes⁷, the OPMP spectroscopy can be performed well for the detection of surface state even in air and does not suffer from the changes of the surface electronic state or doping density as ARPES. On the other hand, our Bi_2Se_3 samples, grown by the modified Bridgman method (see Section S1), have inert properties¹. The TI surface state of the perfectly cleaved (0001) surface of the bulk topological insulator stays intact during a long-term storage in the atmosphere.

S8. Intervalley scattering

The pumping pulses excite the electrons in the Γ valley of Bi_2Se_3 , and a number of them scatter to the L valley, lowering the number of electrons in the Γ valley as shown in Fig. S7. Besides, the electron effective mass m^* in L valley is larger than that in Γ valley due to the smaller curvature of L valley ($1/m^* = \partial^2 E(k)/\partial k^2$). According to the definition of the plasma frequency $\omega_p^2 \equiv 4\pi N e^2 / m^* \epsilon_\infty$ (N is the electron density, m^* is the electron effective mass), both of less electron density and larger effective mass will cause the smaller plasma frequency ω_p , i.e. the red-shift of plasma edge as shown in Fig. S8 which is similar with the case of n-type GaAs⁹. This intervalley scattering is a common phenomenon in semiconductors which has been fully studied in the past. For example, Saeta *et al.*¹⁰ studied the intervalley scattering in GaAs and InP by using far-infrared transmission spectroscopy. They found that the photoexcitation at energies above the X valley minima in GaAs leads to

increased scattering out of the Γ valley and longer return times. Recently, Ho *et al.*¹¹ also investigated the intervalley scattering within a subpicosecond time scale in bulk InAs by using THz pump-THz probe spectroscopy. With a single THz beam excitation on the n-doped InAs at different field strengths, they estimated the electron fractional occupation between the Γ and L valleys. For the common topological insulators, Bi₂Te₃, Bi₂Se₃ etc., they also belong to the narrow bandgap semiconductors. The intervalley scattering ordinarily observed in semiconductors would also naturally take place in both Bi₂Te₃ and Bi₂Se₃. In 1974, Pawlewicz *et al.*¹² had observed the intervalley scattering in Bi₂Te₃ single crystals by measuring the resistivity from 1.3 to 300 K.

After a time scale of several picoseconds, the electrons in the L valley scatter back to Γ valley, which results in the plasma edge of reflectance spectra returns to the original position. Moreover, higher fluence pulses cause more electrons to scatter to the L valley and induce larger effective mass; meanwhile, fewer electrons in the Γ valley. Thus, a larger red-shift can be seen clearly at the photon energy around the plasma edge (~ 136 meV in Fig. S9), where the transient reflectivity changes ($\Delta R/R$) vary from positive to negative. Namely, the sign change of $\Delta R/R$ was observed at lower photon energy (longer wavelength) when Bi₂Se₃ was pumped by higher fluences. This indicates that the higher pumping fluences will cause larger red-shift of the plasma edge. Therefore, the dependence of $\Delta R/R$ curves on the pumping fluences is significantly evident the relation between the $\Delta R/R$ and the red-shift of the plasma edge which is due to the reduction of electron density in the Γ valley and the increase of effective mass in the L valley.

S9. The physical origin of positive signal before 5 ps in $\Delta R/R$

There are two processes for the absorption of the pump beam. One is the interband transition between BVB and BCB and its absorption coefficient α can be estimated by $\alpha = 2\omega k/c = 2.12 \times 10^5 \text{ cm}^{-1}$ (ω is the angular frequency of 800-nm pump beam, $k=2.7$ is the imaginary part of refractive index which is obtained from Fig. S4). The other is the free carrier absorption in BCB and its absorption coefficient α_{free} can be estimated by $\alpha_{\text{free}} = Ne^2/m^* \epsilon_0 n c \tau \omega^2$ (N is the carrier concentration, m^* is

the effective mass, ω is the angular frequency of 800-nm pump beam, τ is the scattering time obtained from FTIR spectra in Fig. S5, n is the real part of refractive index which is obtained from Fig. S4) listed as follows,

Code	n	N (cm ⁻³)	$(1/2\pi)(N/m^*\epsilon_0)^{1/2} = f_p$ (THz)	$1/\tau$ (THz)	α_{free} (cm ⁻¹)
#1	~5.5	-51.5 ± 0.84	172.3	3.66	4.68
#2	~5.5	-13.9 ± 0.26	109.9	3.15	1.64
#3	~5.5	-5.58 ± 0.25	80.0	2.1	0.58
#4	~5.5	-0.25 ± 0.01	24.6	0.99	0.03

The absorption coefficient $\alpha = 2.12 \times 10^5$ cm⁻¹ is much larger than that of $\alpha_{\text{free}} \sim 0.03$ -4.68 cm⁻¹. Thus, the interband transitions between BVB and BCB will dominate the excitation process and induce holes in BVB. Additionally, the imaginary part of refractive index k at 800 nm is insensitive to carrier concentration to cause almost same absorption coefficient. This implies that the total amount of holes in BVB is nearly the same, which will be refilled by the carriers in the Dirac cone. Thus, the negative signal after 5 ps of $\Delta R/R$ is independent of carrier concentration as shown in Fig. S10. The negative signal after 5 ps with low S/N ratio still can be clearly observed on an enlarged scale even for the sample #1 with higher carrier concentration. Usually, this relatively small negative signal after 5 ps is easily smeared out by the large positive signal before 5 ps as shown in the inset of Fig. S10.

The photon energy-dependent positive signal before 5 ps of $\Delta R/R$ can be estimated from the photoinduced red-shift of reflectance spectra in Fig. S8. Within the probing regime (yellow area in Fig. S11) in this study, the amplitude of the positive signal before 5 ps in $\Delta R/R$ is strongly dependent on the carrier concentration, which is qualitatively consistent with the experimental data (symbols in Fig. S11). For the probing photon energy of 141 meV, the amplitude of positive signal before 5 ps in sample #1 is larger than that of sample #4 by at least one order of magnitude. Moreover, the amplitude of positive signal before 5 ps linearly increases as increasing pumping fluences as shown in Fig. S12. However, the amplitude of negative signal after 5 ps also linearly increases as

increasing pumping fluences but saturates when pumping fluence $> 60 \mu\text{J}/\text{cm}^2$. Consequently, the relatively smaller negative signal after 5 ps is easily smeared out at higher pumping fluences.

S10. The physical origin of negative signal after 5 ps in $\Delta R/R$

Since the transmittance spectrum is almost zero (see Fig. S8) in our probing regime, the absorbance spectrum could be simply obtained from reflectance spectrum. However, it is not so straightforward. Therefore, we further estimated the changes of refractive index Δn and Δk after pumping from Fig. S8. According to the formula $\Delta R/R \cong 4\Delta n/(n^2 - 1)$ and $\Delta A/A \propto \Delta k^{13}$, the $\Delta R/R$ and $\Delta A/A$ would be positive and negative, respectively, which explain only the positive signal before 5 ps in our experimental $\Delta R/R$ data but *not* the negative signal. This is because all of above analyses are based on the bulk properties of Bi_2Se_3 . As seen below, these shortcomings came from the analyses based solely on the bulk properties of Bi_2Se_3 .

In order to figure out the origin of negative signal after 5 ps in $\Delta R/R$, we should consider the pure responses from Dirac cone surface state. Graphene is a good example for this concern. Fig. 1(c) in Ref. 14 shows the pump-induced changes $\Delta\epsilon_\tau$ of the in-plane dielectric function of thin graphite at $\tau=0.5$ ps after photoexcitation. Since $\Delta\epsilon_2$ ($\text{Im}\Delta\epsilon_\tau$, the imaginary part of dielectric constant) is the actual physical parameter which describes a change of the state occupancy in the samples. Therefore, $\Delta A/A$ is related to the change of $\Delta\epsilon_2$ when the samples are optically pumped. Additionally, the transient reflectivity changes can be expressed as $\Delta R/R = \alpha_1\Delta\epsilon_1 + \alpha_2\Delta\epsilon_2$, where $\Delta\epsilon_1$ is the real part of dielectric constant, $\Delta\epsilon_2$ is the imaginary part of dielectric constant¹⁵. Generally, $\alpha_1 \cong \alpha_2$ and are positive¹⁵. For the case of graphene, thus, the $\Delta R/R$ is negative and $\Delta A/A$ is positive at the probing frequency below 15 THz. For the case of Bi_2Se_3 , the zero-cross point of $\text{Im}\Delta\epsilon_\tau$ in Fig. 1(c) in Ref. 14 would shift to higher frequency (>37 THz) due to higher E_F in our Bi_2Se_3 . Therefore, the $\Delta R/R$ for Dirac cone surface state in Bi_2Se_3 is negative within our probing region ($21\text{-}37$ THz $\cong 87\text{-}153$ meV), which is consistent with our experimental data, and then the $\Delta A/A$ is positive.

In order to estimate the initial and final density of states in Dirac

cone, we plot the E - k diagram as Fig. S13 by an ARPES band dispersion image of Bi₂Se₃ #2 in Fig. 1. The density of state (DOS) in Dirac cone is energy-dependent and is proportional to the circumference of the dashed rings in Fig. S13, i.e. $\text{DOS} \propto 2\pi R_{\text{Dirac}}$ (R_{Dirac} is the radius of ring). According to Fermi Golden rule, the transition probability $T_{i \rightarrow f} = (2\pi/\hbar)|M_{if}|^2\delta(E_f - E_i - \hbar\omega)$, where M_{if} is dipole matrix element, E_f is the energy of final state, E_i is the energy of initial state, and $\hbar\omega$ is the energy of electromagnetic field. Since $M_{if} = \langle\psi_f|H'|\psi_i\rangle$, where H' is the operator for the interaction between the system and the electromagnetic field, $T_{i \rightarrow f}$ is proportional to DOS in initial and final states, i.e. the $T_{i \rightarrow f} \propto \text{DOS}_i \times \text{DOS}_f \propto 2\pi R_{i,\text{Dirac}} \times 2\pi R_{f,\text{Dirac}}$. Then the amplitude of the photoinduced absorption changes, $|\Delta A/A|$, is proportional to the photoinduced reflectivity changes, $|\Delta R/R|$, which is in turn proportional to the product of initial and final density of states $|\Delta A/A| \propto |\Delta R/R| \propto 2\pi R_{i,\text{Dirac}} \times 2\pi R_{f,\text{Dirac}} \propto R_{i,\text{Dirac}} \times R_{f,\text{Dirac}}$.

Since the transmittance spectrum is almost zero in our probing regime as shown Fig. S8, this indicates that the transient transmissivity changes $\Delta T/T$ cannot be directly performed in our single crystals. Therefore, we take graphene as an example to justify this issue. The positive $\Delta T/T$ and negative $\Delta R/R$ were observed in graphene^{16,17}, which is similar to our experimental results of negative $\Delta R/R$ after 5 ps in Bi₂Se₃ due to the transition process (2) in the Dirac cone surface state. Moreover, if the probing frequency is below the zero-cross point of $\text{Im}\Delta\varepsilon_\tau$ in Fig. 1(c) in Ref. 14, the $\text{Im}\Delta\varepsilon_\tau$ changes from negative to positive and then the $\Delta T/T$ becomes negative. This would be the case of our OPMP study if the transient transmissivity changes $\Delta T/T$ can be performed in Bi₂Se₃ crystals. For the transition process (1) in the bulk state, we know that the $\Delta R/R$ is as a function of Δn (or $\Delta\varepsilon_1$) and Δk (or $\Delta\varepsilon_2$) from above discussions. While the probing frequency is above the plasma edge of 136 meV in Bi₂Se₃ #1, the $\Delta R/R$ will be dominated by the Δn and then the $\Delta R/R$ is positive. According to the formula $\Delta T/T \propto -\Delta k$ ¹³, the $\Delta T/T$ would be positive. Thus, both $\Delta R/R$ and $\Delta T/T$ have same sign for higher probing frequency, which is consistent with the observation in semiconductor InP:Fe¹⁸. Furthermore, if the probing frequency is below the plasma edge of 136 meV in Bi₂Se₃ #1, the $\Delta R/R$ will be dominated by the Δk and then the $\Delta R/R$ becomes negative; meanwhile, the $\Delta T/T$ would be positive. Therefore, $\Delta R/R$ and $\Delta T/T$ have opposite sign for higher probing frequency.

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Figure S1. Schematic diagram of the optical pump mid-infrared probe (OPMP) system.

Figure S2. Characterization of the mid-infrared pulses. (a) Normalized spectra of the mid-infrared pulses for various incident angles of 800-nm-pumping pulses on GaSe crystals. (b) Mid-IR pulse energies and center wavelengths as a function of the incident angles of 800-nm-pumping pulses.

Figure S3. OPMP result of Germanium with probe beam wavelength of 13.7 μm . (a) $\Delta R/R$ as function of delay time and a fitting curve. (b) Differentiated result of the fitting curve shown in (a), whose FWHM gives the temporal resolution of about 500 fs.

Figure S4. Reflectivity measurement at 800 nm for s- and p-polarizations in Bi₂Se₃ #2. Solid lines are global fitting curves using complex Fresnel equations. Fitting gives $Re[n]=5.5$ and $Im[n]=2.7$.

Figure S5. Reflectance spectra (solid lines) of all Bi₂Se₃ used in this study. Dashed lines: fitting by the by a Drude model.

Figure S6. Penetration depth of all Bi₂Se₃ used in this study.

Figure S7. Schematic intervalley scattering from Γ valley to L valley in Bi_2Se_3 .⁸

Figure S8. Transmittance and reflectance spectra of Bi_2Se_3 #1 before pumping (solid line, experimental data) and after pumping (dashed line, which was estimated by the change of effective mass m^* in Fig. S7 and fixed electron density N).

Figure S9. Pumping fluence dependence of $\Delta R/R$ in Bi_2Se_3 #1. (a) Pumping fluence = $113 \mu\text{J}/\text{cm}^2$, (b) pumping fluence = $38 \mu\text{J}/\text{cm}^2$.

Figure S10. The transient reflectivity changes $\Delta R/R$ of Bi_2Se_3 #1 on an enlarged scale of the inset.

Figure S11. Simulated $\Delta R/R$ as a function of photon energy (solid lines) which was estimated from the difference between the reflectance spectra before and after pumping in Fig. S8. Experimental data: the peak amplitude of $\Delta R/R$ before 5 ps (solid and opened symbols) obtained from Fig. 2b.

Figure S12. The peak (Positive: before 5 ps. Negative: after 5 ps.) amplitude of $\Delta R/R$ as a function of pumping fluences in Bi_2Se_3 #4 with probing photon energy of 141 meV.

Figure S13. E - k diagram plotted by an ARPES band dispersion image of Bi_2Se_3 #2 in Fig. 1.