Snapshots of Dirac Fermions near the Dirac Point in Topological Insulators


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Supporting Information

ABSTRACT: The recent focus on topological insulators is due to the scientific interest in the new state of quantum matter as well as the technology potential for a new generation of THz optoelectronics, spintronics and quantum computations. It is important to elucidate the dynamics of the Dirac fermions in the topologically protected surface state. Hence we utilized a novel ultrafast optical pump mid-infrared probe to explore the dynamics of Dirac fermions near the Dirac point. The femtosecond snapshots of the relaxation process were revealed by the ultrafast optics. Specifically, the Dirac fermion-phonon coupling strength in the Dirac cone was found to increase from 0.08 to 0.19 while Dirac fermions were away from the Dirac point into higher energy states. Further, the energy-resolved transient reflectivity spectra disclosed the energy loss rate of Dirac fermions at room temperature was about 1 meV/ps. These results are crucial to the design of Dirac fermion devices.

KEYWORDS: Topological insulator, ultrafast optical pump mid-infrared probe spectroscopy, Dirac fermion dynamics, Dirac fermion-phonon coupling

The discovery of 3D topological insulators (TIs)1 initiated a new era of condensed matter physics.2,3 As Dirac fermions play a crucial role in determining the performances of any real TI devices, a better understanding of the bulk state and the surface state,4−14 and the coupling mechanisms between them, is imperative. From a practical point of view, contact-free optical techniques, such as second harmonic generation,11 terahertz time-domain spectroscopy,15 UV−visible−IR reflectance and transmission spectroscopy,16 and optical pump−probe spectroscopy,17−21 would be the most feasible schemes to investigate the characteristics of TIs. However, the surface signatures are easily overwhelmed by the bulk contributions. Recent TrARPES studies have shown the surface carrier

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population in TIs can be induced by photoexcitation\textsuperscript{12,13} and can separately obtain the temperature and chemical potential relaxation of both the surface and the bulk.\textsuperscript{14} Nevertheless, the ultrafast behavior of Dirac fermions near the Dirac point and their detailed energy-dependent coupling with phonons remain elusive for lack of probes with the appropriate energy range (~100 meV) specific to the Dirac cone. We further take the advantage of the appropriate probe photon energies in the optical pump mid-infrared probe (OPMP) spectroscopy to explore the nonequilibrium dynamics of TIs. The mid-infrared optical pump mid-infrared probe (OPMP) spectroscopy to advantage of the appropriate probe photon energies in the (elusive for lack of probes with the appropriate energy range, as listed in Table 1, (#1: \( n = 5.15 \times 10^{18} \text{ cm}^{-3} \), #2: \( n = 13.9 \times 10^{18} \text{ cm}^{-3} \)), #3: \( n = 5.58 \times 10^{18} \text{ cm}^{-3} \), #4: \( n = 0.25 \times 10^{18} \text{ cm}^{-3} \)) and show corresponding ARPES images.\textsuperscript{24} Details of Bi\(_2\)Se\(_3\) single crystal preparation and the OPMP spectroscopy can be found in the Supporting Information. For the case of Bi\(_2\)Se\(_3\), #1 with a high carrier concentration (\( n = 5.15 \times 10^{18} \text{ cm}^{-3} \)), a positive peak is clearly observed in \( \Delta R/R \). This positive peak gradually diminishes as \( n \) decreases (#1→#4 in Figure 1a). Noticeably, an additional negative peak appears for the cases of \( n = 5.58 \times 10^{18} \text{ cm}^{-3} \) and \( n = 0.25 \times 10^{18} \text{ cm}^{-3} \), and its amplitude is inversely proportional to \( n \).

![Figure 1. Carrier concentration (\( n \)) dependence of the transient change in reflectivity \( \Delta R/R \) in Bi\(_2\)Se\(_3\) single crystals. (a) \( \Delta R/R \) of samples #1 (\( n = 5.15 \times 10^{18} \text{ cm}^{-3} \)), #2 (\( n = 13.9 \times 10^{18} \text{ cm}^{-3} \)), #3 (\( n = 5.58 \times 10^{18} \text{ cm}^{-3} \)), and #4 (\( n = 0.25 \times 10^{18} \text{ cm}^{-3} \)) with a pumping fluence of \( 34 \mu J/cm^2 \) and probing photon energy of 141 meV. (b) ARPES band dispersion images on samples of (a).\textsuperscript{24}](Image 67x273 to 293x496)

Table 1. Fermi Energy and Carrier Concentration of Bulk and Surface States for Various Samples Grown by Different Methods (*Vertical Bridgman, b Modified Floating Zone*)

<table>
<thead>
<tr>
<th>code</th>
<th>( E_F - E_{\text{Dirac, point}} ) (meV)</th>
<th>( n_{\text{bulk}} ) ( \times 10^{18} \text{ cm}^{-3} )</th>
<th>( n_{\text{surface}} ) ( \times 10^{18} \text{ cm}^{-3} )</th>
<th>( n_{\text{bulk}} ) / ( n_{\text{surface}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>422</td>
<td>( -5.15 \pm 0.84 )</td>
<td>( -1.45 )</td>
<td>0.11</td>
</tr>
<tr>
<td>#2</td>
<td>325</td>
<td>( -13.9 \pm 0.26 )</td>
<td>( -0.83 )</td>
<td>0.20</td>
</tr>
<tr>
<td>#3</td>
<td>284</td>
<td>( -5.58 \pm 0.25 )</td>
<td>( -0.72 )</td>
<td>0.35</td>
</tr>
<tr>
<td>#4</td>
<td>260</td>
<td>( -0.25 \pm 0.01 )</td>
<td>( -0.47 )</td>
<td>0.89</td>
</tr>
</tbody>
</table>

\( ^* \text{All samples are n-type. \( d = 23.5 \text{ nm} \) is the penetration depth of 800-nm pumping light (see Supporting Information).} \)

To elucidate the origins of both the positive and negative signals, a model is shown in Figure 2a for the optical pumping (1.55 eV) and mid-infrared probing processes in the schematic energy band structure of the TIs based on the ARPES image in Figure 1b. Because the used probe photon energy (87–153 meV) of the mid-infrared (mid-IR) is much smaller than the band gap of ~300 meV in Bi\(_2\)Se\(_3\) (as shown in the ARPES images of Figure 1b), the interband transitions between the valence band (VB) and the conduction band (CB) of the bulk are not allowed to occur. Thus, the free carrier absorption in the CB (mid-IR probe (1) in Figure 2a) and Dirac cone surface state (mid-IR probe (2) in Figure 2a) will dominate the probe processes, which are responsible for the positive and negative peaks in \( \Delta R/R \), respectively. To confirm this assignment and reveal the physical meanings of the positive peak in \( \Delta R/R \), the photon energy dependence of \( \Delta R/R \) for #1 sample is shown in Figure 2b. By decreasing the photon energy, \( \Delta R/R \) gradually changes from positive to negative. Around 136 meV (1100 cm\(^{-1}\)), there are some intermediate signals mixed with both positive and negative peaks, corresponding to deep in the Fourier transform infrared (FTIR) reflectance spectrum (the inset of Figure 2b). After pumping, the excited carriers suffer the so-called intervalley scattering (see Supporting Information), leading to the redshift of the reflectance spectra. Therefore, the reflectivity increases as a function of time with a large probing photon energy, which is higher than the position of 136 meV deep in the reflectance spectra due to plasma edge. On the contrary, the reflectivity decreases as a function of time with a small probing photon energy, which is lower than the position of 136 meV deep in the reflectance spectra. Similar results were also observed in a typical semiconductor n-type GaAs.\textsuperscript{25}

Comparing the \( \Delta R/R \) curves and ARPES images in Figure 1, the amplitude of the positive peak in \( \Delta R/R \) gradually shrinks as the bulk carrier concentration decreases (see Table 1). On the other hand, the negative peak in \( \Delta R/R \) increases as the bulk and surface carrier concentrations decrease. However, the negative peak of \( \Delta R/R \) increases dramatically with an increasing ratio of the surface carrier concentration to the total carrier concentration \( n_{\text{surface}} / (n_{\text{surface}} + n_{\text{bulk}}) \) in Table 1, implying an intimate relation between the negative peak of \( \Delta R/R \) and Dirac fermions. Besides, the \( \Delta R/R \) signal significantly depends on the pumping fluorences shown in Figure 3a. Interestingly, the positive peak of \( \Delta R/R \) has a stronger dependence on the pumping fluorences than the negative peak does. Therefore, the negative peak still subsists at the low pumping fluence of 3.3 \( \mu J/cm^2 \),\textsuperscript{26} while the positive peak almost vanishes. This means the mid-IR probe process (1) in the bulk state (see Figure 2a) can be suppressed by reducing

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the pumping fluences; meanwhile, the mid-IR probe process (2) (see Figure 2a) associated with the negative peak can be preserved at the low pumping fluence (see Supporting Information). Here, we can conclude that the positive (or negative) signal within a several picoseconds time scale in $\Delta R/R$ is due to the process (1) of the mid-IR probe in the bulk state of Bi$_2$Se$_3$.

The relation between the negative peak and Dirac fermions can be certified in a quantitative way. According to the Fermi Golden rule, the amplitude of the negative peak should be proportional to the transition probability ($T_{i\rightarrow f}$) between the initial and final density of states in the Dirac cone. With an increase in the probing photon energy, the amplitude of the negative peak increases. Owing to the large positive signal before 5 ps in samples #1 and #2, this probing photon energy dependence of the negative peak amplitude cannot be easily disclosed. However, this dependence was clearly observed in both samples #3 and #4. The experimental data are fitted well by the $R_{i,\text{Dirac}} \times R_{f,\text{Dirac}}$ (dashed line in Figure 3c, $R_{i,\text{Dirac}}$ and $R_{f,\text{Dirac}}$ are the circumferences of rings in Figure 2a), which is proportional to the transition rate between the initial and final density of states for the mid-IR probe process (2) in the Dirac cone (see Supporting Information). This strongly indicates the negative peak of $\Delta R/R$ is dominated by the mid-IR probe process (2) in the Dirac cone (see Figure 2a). Consequently, the ultrafast dynamics of the Dirac fermions can be clearly disclosed by the negative peak of $\Delta R/R$. The above experiments were carried out at the low pumping fluence of 3.3 $\mu$J/cm$^2$ to avoid disturbance of the positive peak from the bulk state, as shown in Figure 3b.

The rising time ($\tau_r$) and decay time ($\tau_d$) of the negative peak of $\Delta R/R$ significantly depends on the probing photon energy, as in Figure 3d. The rising time of the negative peak of $\Delta R/R$ also becomes longer when the probed regime is closer to the Dirac point. On the basis of the above observations, we can further establish the ultrafast relaxation picture for Dirac fermions in TIs. Immediately following the 1.55 eV pumping, the major process is the carriers in the bulk valence band (BVB) are excited to the bulk conduction band (BCB). The carrier recombination between the BCB and BVB can be ignored in this study due to the time scale for such a process is typically $\gg$1 ns. Consequently, the unoccupied states in BVB caused by pumping would mainly be refilled through the bottom part of the upper Dirac cone that almost overlaps with the top of BVB at the same momentum space, as shown in the ARPES images of Figure 1b. This implies the carriers in this part of the Dirac cone can be easily transferred into the unoccupied states in BVB and increasing the number of the unoccupied states near the Dirac point enhances the absorption channel for the mid-IR process (2) in the Dirac cone (Figure 2a). Therefore, the reflectivity of the mid-IR probing light decreases within 1.47–3.60 ps, that is, the rising time of the negative peak in Figure 3b,d. Once the carriers in the Dirac cone relax into BVB, the BCB (like a carrier reservoir) subsequently injects the excited carriers into the unoccupied states in the Dirac cone to diminish the absorption channel for the mid-IR process (2) (Figure 2a). This leads to the increased mid-IR reflectivity within 14.8–87.2 ps, consistent with the ARPES results of a nonequilibrium population of the surface state persisting for $>10$ ps. The several tens of picoseconds in decay time, which is much longer than the rising time of several picoseconds, is because the carriers in BCB cannot directly transfer into the top of the Dirac cone without overlaps occurring between them and other auxiliaries, for example, phonons. A movie showing the relaxation processes of Dirac fermions in the Dirac cone after pumping is included in the Supporting Information.
Phonons have been considered as the main medium in the relaxation of Dirac fermions. Here, we follow this approach. The photon energy dependence of the rising time implies the coupling strength ($\lambda$) between Dirac fermions and phonons varies at different positions of the Dirac cone. According to the second moment of the Eliashberg function, the $\lambda$ is inversely proportional to the relaxation time ($\tau_e$) of excited electrons

$$\langle \omega^2 \rangle \propto \frac{1}{\tau_e}$$

(1)

where $\omega$ is the phonon energy that couples with the electrons. For the estimate of $\langle \omega^2 \rangle$, some vibrational modes are more efficiently coupled to Dirac fermions than others are. In the case of Bi$_2$Se$_3$, the symmetric $A_{1g}$ mode of $\sim$8.9 meV is coherently excited by photoexcitation and efficiently coupled. Taking $\tau_e = \tau_i$ in Figure 3d and $T_e = 370$ K (obtained from ref 14 at the low pumping fluence as mentioned above) to estimate the coefficient of $(\pi k_B T_e/3\hbar)$ in eq 1, the photon energy dependence of the Dirac fermion-phonon coupling strength is $\lambda = 0.08$ to 0.19, as shown in Figure 4a. Recently, the ARPES measurements have reported inconsistent electron-phonon coupling strength in Bi$_2$Se$_3$ varying from a rather small $\lambda \sim 0.08$ to a larger $\lambda \sim 0.25$. The Dirac fermion-phonon coupling strength measured by the present OPMP becomes significantly smaller near the Dirac point (the point of $K_f = 0$ in Figure 4a), which has a qualitatively similar tendency to the estimate of equation 8 (dashed line in Figure 4a) in ref 29. The present results suggest that the variation of $\lambda$ from ARPES may be due to the different explored regimes (i.e., the different chemical potentials) in the Dirac cone. Besides, the time-resolved ARPES experiments also showed similar results. Wang et al. reported that the surface cooling rate decrease with the Fermi level (i.e., closing to the Dirac point). Because the cooling time is inversely proportional to the surface cooling rate, these time-resolved ARPES results are consistent with those in Figure 3d. If the Dirac fermions are closer to the Dirac point, they will have weaker coupling with the phonons to suppress the scattering with phonons. This also implies the effective mass of Dirac fermions in the surface state gradually decreases as the Dirac fermions approach the Dirac point, in agreement with the results in graphene. Consequently, this study further provides a possibility to control the characteristics of Dirac fermions for various applications in TIs such as terahertz optoelectronics, spintronics, quantum computation, and magnetic memories.

![Figure 3. Pumping fluence and photon energy dependence of $\Delta R/R$ and its amplitude and rising (decay) time in the surface state. (a) With probing photon energy of 141 meV, the $\Delta R/R$ of Bi$_2$Se$_3$ #4 at various pumping fluences from 3.3–105 $\mu$J/cm$^2$. (b) With a pumping fluence of 3.3 $\mu$J/cm$^2$, the $\Delta R/R$ of Bi$_2$Se$_3$ #4 at various photon energies from 90–152 meV. (c) The photon energy-dependent negative peak amplitude of $\Delta R/R$ in panel b. The photon energy dependence of the normalized absorption probability (dashed line, that is, $R_{\text{Dirac}} \times R_{\text{Dirac}}$ in Figure 2a) of the mid-IR probe beam in the Dirac cone surface state. (d) The photon energy-dependent rising time ($\tau_r$) and decay time ($\tau_d$) of $\Delta R/R$ in (b).](dx.doi.org/10.1021/nl4021842)
first moment, \((\int (\Delta R/R) E_{\text{photon}} dE_{\text{photon}})/(\int (\Delta R/R)dE_{\text{photon}})\), we estimate the energy loss rate of carriers in the Dirac cone. As shown in Figure 4b, the solid dots represent the first moment at different time, which is associated with the red shift of the absorption peak in Figure 4b. An exponential fit to the time-dependent first moment in Figure 4b gives a relaxation time of 14.8 ps within the range of 15 meV. Therefore, the energy loss rate of Dirac fermions in the Dirac cone is \(\sim 1\) meV/ps, which is larger than that of \(\sim 0.64\) meV/ps in GaAs estimated from ref 25 but smaller than that of \(\sim 17.7\) meV/ps in graphene with Dirac cone. This parameter measured by OPMP would be extremely important for designing optoelectronics, especially in the terahertz range.

ASSOCIATED CONTENT

Supporting Information
Sample preparation and experimental details on optical pump mid-infrared probe spectroscopy. Angle-resolved photoemission spectroscopy and determining the carrier concentration of surface and bulk states. The physical origin of positive and negative signals in \(\Delta R/R\). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

that most carriers in BCB and surface states still keep discussed in the section S9 of Supporting Information. This indicates transitions between BVB and BCB dominate the excitation process as perturbation limit and the linear response. Additionally, the interband pumping.

experiment13 has demonstrated that the phonon-assisted cooling of population in Dirac cone observed by time-resolved ARPES Phys. Rev. Lett. terahertz spectroscopy.


(21) Chen, H.-J.; et al. Phonon dynamics in Cu,Bi2Se3 (x = 0, 0.1, 0.125) and Bi2Se3 crystals studied using femtosecond spectroscopy. Appl. Phys. Lett. 2012, 101, 121912.


(26) If one absorbed photon generates one photoinduced carrier, the maximum photoinduced carrier density can be estimated by ∆n = (1 – R) × F/(E × δ), where R = 0.55 is the reflectance, F = 3.3 μJ/cm² is pumping fluence, E = 2.48 × 10−19 J (= 1.55 eV) is the pumping photon energy, δ = 23.5 nm is the penetration depth. For the pumping fluence of 3.3 μJ/cm², the photoinduced carrier density ∆n is around 2.54 × 10¹⁵ cm⁻³. Figure S12 in Supporting Information further shows that the pump–probe experiments were performed at the weak perturbation limit and the linear response. Additionally, the interband transitions between BVB and BCB dominate the excitation process as discussed in the section S9 of Supporting Information. This indicates that most carriers in BCB and surface states still keep “cold” during pumping.

(27) The electrons and holes in Dirac cone also possibly recombine cross the Dirac point. However, the asymmetric decay of carrier population in Dirac cone observed by time-resolved ARPES experiment13 has demonstrated that the phonon-assisted cooling of hot carriers is the main relaxation process, which is the focus point in this study.


