

Ultrafast All-Optical Terahertz Switchable Modulation Using Van Der Waals $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ Heterostructures

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2D all-van der Waals Fe_nGeTe_2 /topological insulator heterostructures present compelling prospects for the development of advanced opto-spintronic devices, attributed to the coupling between ferromagnetic and topological characteristics. The ultrafast laser-induced terahertz (THz) switchable modulations in $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures are investigated by employing optical pump-THz probe (OPTP) spectroscopy. By comparing the OPTP results of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ with those obtained from single Fe_4GeTe_2 and Bi_2Te_3 films, it is found that the optically-induced THz modulation is attributed to both interface carrier accumulation and thermal effect in Fe_4GeTe_2 . Furthermore, the thickness- and temperature-dependent measurements enable the establish comprehensive rules governing the switching of photoconductivity from positive to negative. The findings highlight a promising pathway for optically controlled THz modulators, achieved by modulating charge dynamics at temperatures near the topological-to-trivial transition in all-van der Waals ferromagnetic Fe_4GeTe_2 /topological insulator heterostructures.

1. Introduction

Terahertz (THz) technology holds extensive application prospects in high-speed communications, radar imaging, biological detection, and fundamental research.^[1–5] Notably, THz modulators are key components in THz technology, actively controlling the intensity, polarization, and phase of THz waves, which significantly influence their practical applications.^[6–13] In recent decades, van der Waals (vdW) heterostructures have demonstrated potential for combining high charge carrier mobility with high optical absorption, thereby opening up new avenues for the development of high-performance optoelectronic applications.^[14–18] Especially, vdW heterostructure-based THz modulators have garnered significant attention for their optical control capabilities. This

approach offers a higher degree of freedom and manipulation of THz waves, attributed to its rapid response and non-invasive nature.^[19–22] Conventionally, the transmitted THz waves are substantially attenuated under laser excitation. For multi-state modulating applications, it is imperative to identify suitable 2D materials that can enhance the transmission of THz waves when illuminated by light.

The recently discovered 2D vdW magnets, with tunable characteristics and interlayer coupling, offer a novel platform. Their magnetic and electrical properties can be modulated not only by thickness,^[23] and atomic composition,^[24] but also by various external factors, including strain, voltage, magnetic field, and light absorption.^[25–30] On the one hand, Liu et al. demonstrated that the magnetization of Fe_3GeTe_2 can be strongly modulated by femtosecond laser pulses.^[31] Gong et al. reported that the magnon amplitude, frequency, and lifetime in $\text{Fe}_{3.6}\text{Co}_{1.4}\text{GeTe}_2$ can be controlled using laser polarization.^[32] On the other hand, Ma et al. demonstrated a broad-spectrum negative photoconductivity of ferromagnetic $\text{Fe}_3\text{GeTe}_2/\text{O-Fe}_3\text{GeTe}_2$ heterostructure, which is due to the semimetal/oxidation interface-assisted dual-response mechanism.^[33] L. Tomarchio et al. discovered a correlation between magnetic order and THz electrodynamics in both Fe_3GeTe_2 and Fe_5GeTe_2 films.^[34] The coexistence of both positive photoconductivity (PPC) and negative photoconductivity (NPC) in one material enhances its technological potential, particularly in the conceptualization of logic gates for controlling data

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processing. However, the THz modulation depth of Fe_3GeTe_2 is only $\approx 1\%$,^[34] which limits its practical application. Hence, 2D vdW magnets with large modulation depth, ultrafast response, and switchable are desired for the fabrication of an ultrafast THz modulator, which has potential applications in high-speed communication and data processing.^[35,36]

It is noted that the ferromagnetism of a 2D vdW magnet can be tailored through interfacial engineering.^[37] For instance, Wang et al. demonstrated that the interfacial coupling between Fe_4GeTe_2 and sapphire substrates can increase the Curie temperature (T_c) of Fe_4GeTe_2 to 530 K.^[38] In the heterostructure combining a ferromagnetic insulator EuS with Bi_2Se_3 , the ferromagnetism can persist up to room temperature.^[39] Additionally, Wang et al. demonstrated that the T_c of $\text{Fe}_3\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures is enhanced up to 400 K.^[40] These 3D topological insulators, such as Bi_2Se_3 and Bi_2Te_3 , are characterized by a conducting surface state and an insulating bulk band gap. Bi_2Se_3 and Bi_2Te_3 have shown great potential for thermoelectric devices and THz optoelectronics due to their superior properties, such as broadband spectral absorption, high carrier mobility, and strong light-matter interaction.^[41–44] Recently, the combination of Fe_nGeTe_2 with topological insulators has emerged as a promising candidate for novel opto-spintronic devices.^[45] For example, THz spins current bursts have been observed in the 2D vdW $\text{Fe}_3\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ due to spin-to-charge conversion induced by the inverse Edelstein effect.^[46] The helicity-dependent photocurrents have been induced by the interface coupling between Fe_4GeTe_2 and Bi_2Te_3 , primarily governed by the circular photogalvanic effect.^[47]

The control of materials' conductivity using light on ultrafast time scales can provide fundamental insights into transient electronic processes, such as charge excitation and transfer,^[48–50] as well as the subsequent interactions between electrons and lattice or spin degrees of freedom.^[51–55] Understanding the photoconductivity dynamics in 2D vdW Fe_nGeTe_2 /topological insulator heterostructures allows shedding light on the interaction between the electronic, lattice, and magnetic degrees of freedom in view of their applications in switchable THz modulation. In this work, we investigate the optically-induced THz modulation of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures grown on sapphire substrates using optical pump-THz probe (OPTP) spectroscopy. Our experimental results demonstrate that the THz photoconductivity of a single Bi_2Te_3 film shows a positive and fast relaxation response in the tens of picosecond time scale. While the THz photoconductivity of a single Fe_4GeTe_2 film shows a negative and slow response in the hundreds of picosecond time scales. In contrast, for a Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 (8 nm) heterostructure, the THz photoconductive is enhanced by an order of magnitude and shows an ultrafast response with a time constant of ≈ 1.0 ps under identical photoexcitation. This ultrafast THz modulation in $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure is derived from the increased carrier scattering between the photocarrier with surface states of the Bi_2Te_3 film, which decreases the mobility of the photocarrier significantly. Furthermore, we systematically demonstrate the switchable THz photoconductivity of these heterostructures by varying thickness, pump fluence, and temperature. All analyses and conclusions drawn in this study are based on the raw data, without any influence from theoretical modeling or fitting procedures. Our OPTP finding in this work demon-

strates an alternative method for the development of all-optical ultrafast THz modulators, opto-logic gates, and multi-bit memory devices based on 2D vdW ferromagnet/topological insulator heterostructures.

2. Experimental Results and Discussion

The detailed fabrication procedures for Fe_4GeTe_2 , Bi_2Te_3 , and $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures on sapphire substrates are described in the Experimental Section. **Figure 1a** illustrates the geometric configuration of the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted to characterize the layered structure of the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure, as shown in **Figure 1b**. The HAADF-STEM image clearly exhibits two distinct contrast regions, corresponding to the Fe_4GeTe_2 (top layer) and Bi_2Te_3 (bottom layer), with contrast differences arising from the varying atomic numbers of the constituent elements. X-ray diffraction (XRD) measurements were performed to analyze the crystal structure. In **Figure 1c**, the XRD pattern of Fe_4GeTe_2 exhibits peaks at 9° , 18.2° , 27.4° , 38.1° , and 56.4° , corresponding to the (003), (006), (009), (0012), and (0018) plane, respectively. In **Figure 1d**, the XRD pattern of Bi_2Te_3 shows peaks at 8.6° , 17.5° , 44.7° , and 54.2° , corresponding to the (003), (006), (0015), and (0018) plane, respectively. In **Figure 1e**, for the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure, the peaks are observed at 9° and 18.4° corresponding to (003) and (006) plane of Bi_2Te_3 and Fe_4GeTe_2 , respectively. The peak observed at 27.6° corresponds to (009) plane of Fe_4GeTe_2 . The peaks at 45.1° and 53.2° correspond to (0015) and (0018) plane of Bi_2Te_3 , respectively. The peak at 56.9° corresponds to (0018) plane of Fe_4GeTe_2 . The peak at 41.7° corresponds to (006) plane of Al_2O_3 substrate. It is observed that the peaks of Fe_4GeTe_2 within the heterostructures are red-shifted compared to those of the pure Fe_4GeTe_2 film. This indicates that a compressive strain is generated along the growth direction, consistent with the fact that the lattice constant of Bi_2Te_3 (4.34 Å) is larger than that of Fe_4GeTe_2 (4.04 Å).^[40,56] All characterization results demonstrate the high crystalline quality and smooth surface of the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures grown on Al_2O_3 substrate via molecular beam epitaxy (MBE).

The THz transmission properties of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures were first investigated using broadband THz time-domain spectroscopy (THz-TDS) in a transmission configuration, further details are provided in the Experimental Section. As depicted in **Figure 1f**, the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure exhibits a transmission of $\approx 88\%$ measured at 0.5 THz without photoexcitation, resulting in an insertion loss of -1.11 dB compared to the case without the heterostructure. The THz transmittance decreases as the thickness of Fe_4GeTe_2 film increases.

In the following, we utilized the standard OPTP spectroscopy to investigate the photo-induced modulation of THz transmission in $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures. The OPTP spectroscopy setup, employing 800 nm (photon energy of 1.55 eV) photo-excitation, is illustrated in **Figure 2a**. Two delay lines were used to adjust the time delay between the optical pump and THz probe pulse through the sample, as well as the THz

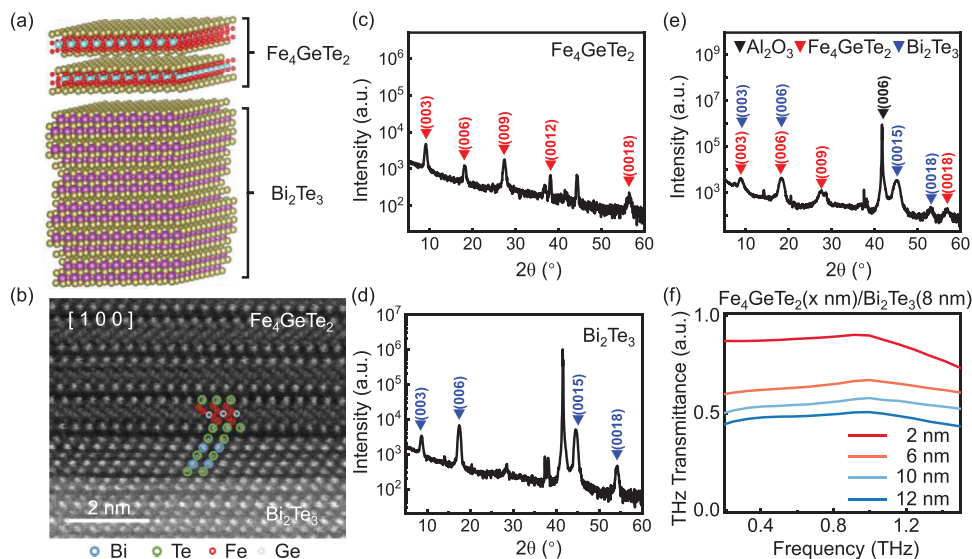


Figure 1. Characterization of Fe₄GeTe₂/Bi₂Te₃ heterostructure. a) Schematic illustration of the crystal structure of the Fe₄GeTe₂/Bi₂Te₃ heterostructure. b) Cross-section high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Fe₄GeTe₂/Bi₂Te₃, providing a clear distinction between the two materials within the heterostructure. The scale bar represents 2 nm. The blue, green, red, and yellow circles denote Bi, Te, Fe, and Ge atoms, respectively. XRD patterns of c) Fe₄GeTe₂ film, d) Bi₂Te₃ film, and e) Fe₄GeTe₂/Bi₂Te₃ heterostructures. f) The THz transmittance spectra of the Fe₄GeTe₂ (2, 6, 10, 12 nm)/Bi₂Te₃ (8 nm) heterostructures grown on sapphire substrate.

probe pulse and the optical gating pulse on an electro-optical detector ZnTe. Further details are provided in the Experimental Section. By varying the delay time Δt between the optical pump beam and the THz probe pulse, we recorded the photo-induced transient change in THz transmission as $-\Delta E/E_0(\Delta t) = -(E(\Delta t) - E_0)/E_0$, where E_0 and E are the THz peak values before and after the photoexcitation, respectively. This allows for further determination of the dynamical THz modulation. In the thin-film approximation, $-\Delta E/E_0(\Delta t)$ is proportional to the photoconductivity $\Delta\sigma(\Delta t) \propto -\Delta E/E_0(\Delta t)$. The negative value of $\Delta E/E_0(\Delta t)$ indicates a PPC. Both the sign and temporal evolution of photoconductivity are governed by changes in carrier density Δn and/or mobility $\Delta\mu$, expressed as $\Delta\sigma = e\Delta n\Delta\mu$, with e is the electron charge. The dynamics of photoconductivity are crucial for light-electric interconversion in photoelectronic applications.^[57–61]

It is instructive to compare the typical dynamics of $-\Delta E/E_0(\Delta t)$ for Fe₄GeTe₂ film, Bi₂Te₃ film, and Fe₄GeTe₂/Bi₂Te₃ heterostructures at 300 K, when excited by a 0.56 mJ/cm² linearly polarized pulse at 800 nm, as illustrated in Figure 2b,d,e, respectively. Figure 2b shows the $-\Delta E/E_0(\Delta t)$ the behavior of a 4 nm Fe₄GeTe₂ thin film under different magnetic field conditions: +H (red circles), −H (green circles), and no external magnetic field (blue circles). Upon the photoexcitation, the 800 nm laser pulses enhance the transmission of the THz pulses transmitted through the Fe₄GeTe₂ film, which exhibits THz NPC. The recovery dynamics of $-\Delta E/E_0(\Delta t)$ exhibit long-time scales on the order of hundreds of picoseconds.

To understand the THz NPC effect, several possible mechanisms are discussed. First, the interaction between the photoinduced surface plasmon polariton and the electrons can introduce additional scattering channels, thereby reducing current flow.^[62,63] However, the real part of the conductivity is positive,

which indicates that the electromagnetic field cannot be effectively localized on the surface of Fe₄GeTe₂, thus ruling out the surface plasmon polariton effect. Second, the 4 nm Fe₄GeTe₂ film remains in a ferromagnetic phase at room temperature ($T_c \approx 530$ K). Thus, the interaction of femtosecond laser pulses with the Fe₄GeTe₂ film can induce an out-of-equilibrium ultrafast demagnetization.^[64] The ultrafast demagnetization is also verified by the observation of THz pulse generation signals overlapping with the OPTP signals, as shown in Figure 2c. As expected, reversing the magnetization direction results in a reversal of the THz emission polarity. Even in the absence of an external magnetic field, THz emission signals are still observed, indicating that it originates from the spontaneous magnetization of the sample. However, no obvious changes in time-resolved OPTP traces were observed when an external magnetic field was applied to the heterostructures, as shown in Figure 2b. The THz emission depends strongly on the external magnetic field, whereas the carrier dynamics is magnetic-field independent. In addition, the relaxation of $-\Delta E/E_0(\Delta t)$ over time intervals $\Delta t > 1$ ps primarily capture the characteristics of carrier dynamics. Actually, this NPC was first observed in graphene monolayers produced by chemical vapor deposition methods.^[58,59] Due to the high carrier density of the metallic Fe₄GeTe₂ film, the contribution of Δn is small. Therefore, the NPC can be understood as follows: when a laser pulse is absorbed in the Fe₄GeTe₂ film, the energy from the photons is transferred to the charge carriers. This leads to a rapid thermalization of the electron bath to a higher temperature via electron-electron scattering. This leads to an increase of the scattering rate of electrons and then results in a decrease of the charge mobility and then the negative photoconductivity.^[65] The long relaxation process is related to the electron cooling toward the equilibrium state, corresponding to an increase in the conductivity.

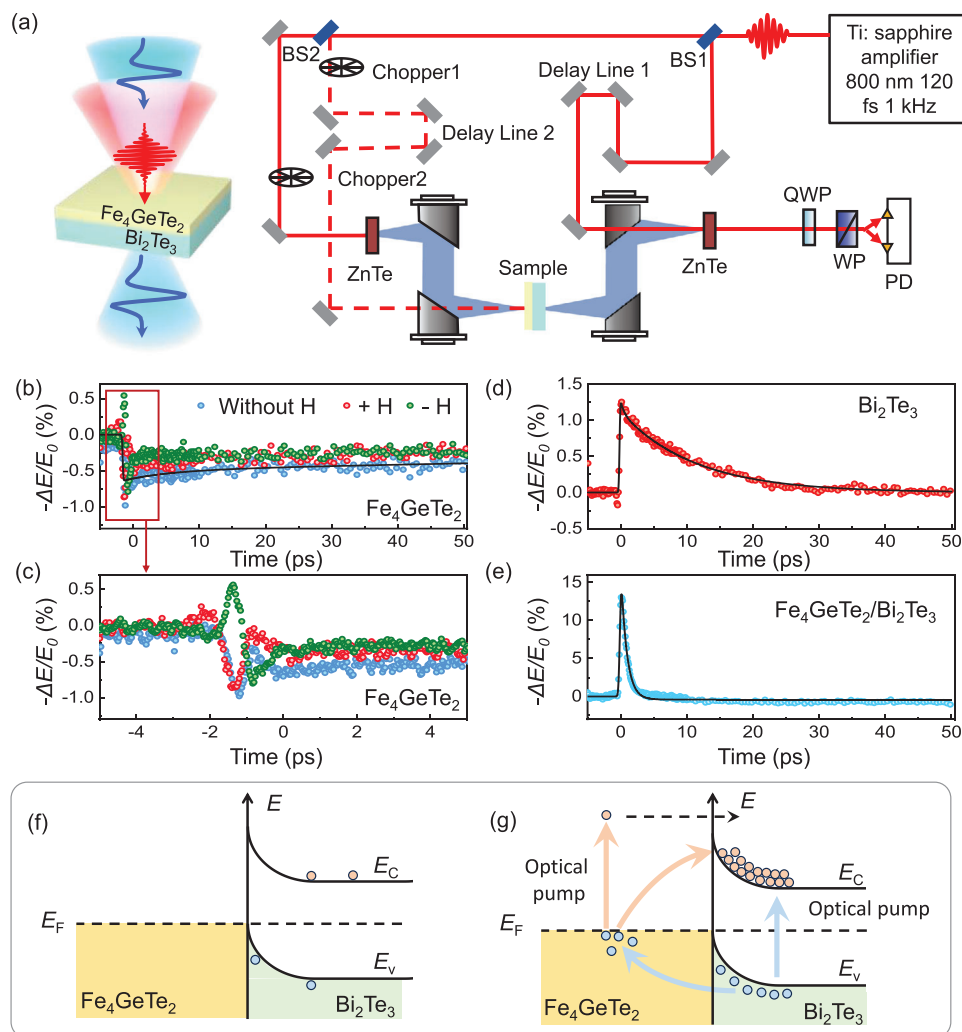


Figure 2. OPTP spectroscopy of Fe₄GeTe₂, Bi₂Te₃, and Fe₄GeTe₂/Bi₂Te₃ films. a) Schematic illustration of the OPTP setup for the Fe₄GeTe₂/Bi₂Te₃ heterostructures. Solid and dashed red lines indicate the optical probe and pump light, respectively, while the blue beam indicates the THz probe pulse. b) Optical modulation of the transmitted THz peak electric fields for pure Fe₄GeTe₂ film (4 nm), measured with $\pm H$ and without H. c) THz emission waveforms were observed in conjunction with the OPTP signals of Fe₄GeTe₂ on short time scales. The photo-modulation of transmitted THz peak electric fields for d) Bi₂Te₃ film (8 nm) and e) Fe₄GeTe₂ (4 nm)/Bi₂Te₃ (8 nm) heterostructures as a function of delay time, measured at 300 K. Solid lines represent fits to a bi-exponential decay function. Proposed band schemes of Fe₄GeTe₂/Bi₂Te₃ heterostructures f) before and g) after laser illumination at room temperature.

In contrast, for an 8 nm thick topological insulator Bi₂Te₃ film, the $-\Delta E/E_0$ (Δt) exhibits an opposite trend, as shown in Figure 2d. The observed increase in the THz photoconductivity indicates that the primary contribution stems from the photo-increase of the carrier population in conduction and valence bands, similarly reported in other topological insulators, such as Sb₂Te₃^[66] and Bi₂Se₃.^[67] It can be found that the value of the modulation depth (MD) for Bi₂Te₃ film, given by $MD = \Delta E_{\max}/E_0 = -1.25\%$, which is more than twice as much as that of Fe₄GeTe₂ under the same pump fluence. Upon photoexcitation, the electrons are excited from the valence band to the conduction band. The hot electrons then rapidly thermalize, cool down, and form a hot Fermi-Dirac distribution in Bi₂Te₃, which takes ≈ 500 fs and corresponds to the rise of $-\Delta E/E_0$ (Δt). To analyze the whole $-\Delta E/E_0$ (Δt) data, the dynamical response can be well repro-

duced with the following function:

$$-\frac{\Delta E}{E_0}(\Delta t) = Ae^{-\frac{\Delta t}{\tau_f}} \left[1 - \operatorname{erf} \left(\frac{\omega}{\tau_f} - \frac{\Delta t}{2\omega} \right) \right] + Be^{-\frac{\Delta t}{\tau_s}} \left[1 - \operatorname{erf} \left(\frac{\omega}{\tau_s} - \frac{\Delta t}{2\omega} \right) \right] \quad (1)$$

where Δt is the delay time between the pump and probe pulse. $\omega = 60$ fs is the rms width of the pulse. A and B represent the coefficients associated with the fast and slow decay components, respectively. τ_f and τ_s are the time constants for fast and slow processes, respectively. Erf is the error function. The extracted time constants were $\tau_f = 0.61 \pm 0.16$ ps and $\tau_s = 11.24 \pm 0.15$ ps (Fitting parameters in Note S1, Supporting Information). Since

the light can penetrate into the Bi_2Te_3 film, both bulk and surface carriers' information can be obtained. The fast component can be assigned to the relaxation of hot carriers from higher energy to the minimum bulk conduction band, while the slow component is attributed to the electron-hole recombination through 1) bulk conduction band to bulk valence band and 2) bulk conduction band to topological surface states.^[68–70]

We now examine the $-\Delta E/E_0$ (Δt) response of the Fe_4GeTe_2 (4 nm)/ Bi_2Te_3 (8 nm) heterostructures, as shown in Figure 2e. The pump laser induces a positive photoconductivity, followed by a rapid recovery to the original transmission value with a time constant $\tau_f = 1.04 \pm 0.02$ ps. This dynamic response exhibits distinct characteristics compared to those of both Bi_2Te_3 and Fe_4GeTe_2 individually, which show much slower relaxation time. The ≈ 1 ps decay rate of the THz photoconductivity can be interpreted as an intra-surface state relaxation rate, not as the lifetime of the massive electrons. Moreover, by forming the heterojunction between Fe_4GeTe_2 and Bi_2Te_3 , the MD increases significantly, reaching 13.1% under the same pump fluence. This significant enhancement is ≈ 1 order of magnitude larger than that measured for the individual constituent materials of Bi_2Te_3 and Fe_4GeTe_2 . The ultrafast and enhanced THz photoconductivity suggests the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure is suitable for fabricating an all-optical control THz modulator. It was also noted that we observed no obvious changes in the OPTP traces when applying an external magnetic field to the heterostructures (see Note S2, Supporting Information).

The proposed band schemes of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructure are illustrated in Figure 2f. Following photoexcitation, hot electron-hole pairs are generated inside the metallic Fe_4GeTe_2 layer. The large number of hot electrons in the Fe_4GeTe_2 layer with excess energy overcome the Schottky barrier and accumulate at the conduction band of the Bi_2Te_3 layer. The separation of electrons and holes can enhance the THz modulation depth. After this process, the electron bath dissipates its energy to both lattice and spin systems, depending on factors such as thermal conductivity, thickness, and substrate properties.

To further investigate the photoinduced THz modulation of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures, we conducted thickness, pump-fluence, and temperature-dependent OPTP measurements. First, we fixed the thickness of the Bi_2Te_3 layer at 8 nm while varying the thickness of the Fe_4GeTe_2 layer (2, 6, 10, and 12 nm). As shown in Figure 3a,b, the time axis is divided into short-time and long-time windows, respectively, to highlight the temporal behaviors. The black curves illustrate the double exponential decay fit to the data using Equation (1), as detailed in Note S3 (Supporting Information). It can be found that the light-induced modulation of THz transmission exhibits a strong dependence on the thickness of the Fe_4GeTe_2 layer. Figure 3c shows the MD changes from -12.5% to $+2.5\%$ with increasing the thickness of the Fe_4GeTe_2 layer from 2 to 12 nm. The Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 and Fe_4GeTe_2 (6 nm)/ Bi_2Te_3 show nearly identical time-resolved dynamics, while the Fe_4GeTe_2 (6 nm)/ Bi_2Te_3 shows a smaller magnitude. When the thickness of the Fe_4GeTe_2 layer increases to 10 nm, an initial increase in photoconductivity is followed by a secondary transition to the negative photoconductivity, as shown by the orange curve in Figure 3b. For the thickest Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 , $-\Delta E/E_0$ (Δt) shows a complete negative photoconductivity with a very slow relaxation back

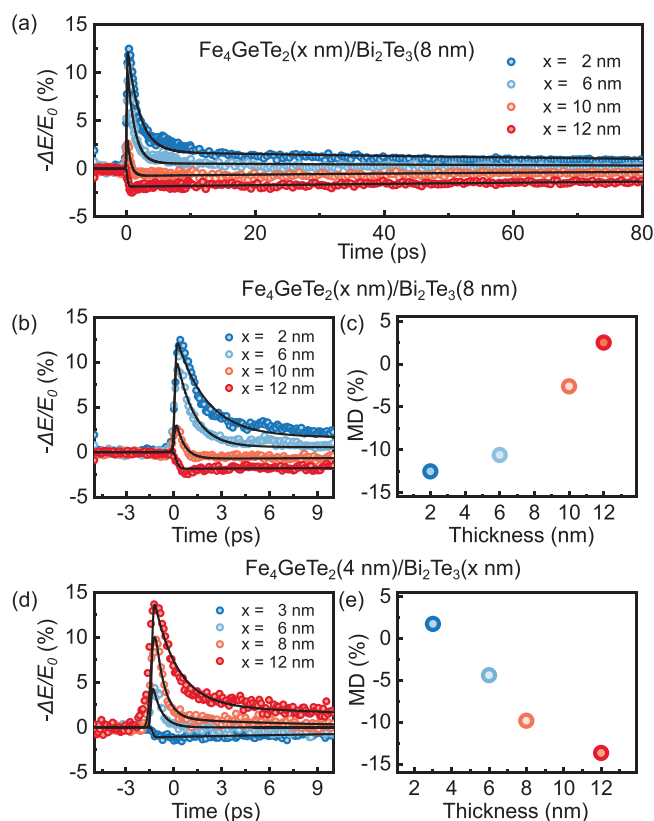


Figure 3. OPTP measurements of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures at different thicknesses at room temperature. a) OPTP signals were measured for Fe_4GeTe_2 (2, 6, 10, 12 nm)/ Bi_2Te_3 (8 nm). b) Initial time windows of the OPTP signals are shown in (a). c) The modulation depth (MD) for Fe_4GeTe_2 (2, 6, 10, 12 nm)/ Bi_2Te_3 (8 nm). d) OPTP signals were measured for Fe_4GeTe_2 (4 nm)/ Bi_2Te_3 (3, 6, 8, 12 nm). e) The MD for Fe_4GeTe_2 (4 nm)/ Bi_2Te_3 (3, 6, 8, 12 nm) heterostructures.

to the equilibrium, which is similar to Fe_4GeTe_2 single layer. It can be found that as the thickness of Fe_4GeTe_2 increases, less light can penetrate (see Note S4, Supporting Information). Consequently, the charge accumulation effect at the interface of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ diminishes, while the thermal effect from the bulk Fe_4GeTe_2 layer becomes dominant. In addition, we also study the effect of Bi_2Te_3 layer thickness on the OPTP signals of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures at room temperature. As shown in Figure 3d, for the Fe_4GeTe_2 (4 nm)/ Bi_2Te_3 (3 nm), the $-\Delta E/E_0$ (Δt) exhibits a complete negative photoconductivity. When the thicknesses of Bi_2Te_3 layer increase above 6 nm, the sign of photoconductive changes from negative to positive. The black curves illustrate the double exponential decay fit to the data using Equation (1), as seen in Note S5 (Supporting Information). In addition, the positive photoconductivity increases monotonously as the thickness of the Bi_2Te_3 layer is increased up to 12 nm. The corresponding MD value changes from $+1.8\%$ to -13.7% as the Bi_2Te_3 layer increases from 3 to 12 nm, as shown in Figure 3e.

Second, to further investigate the effect of pump fluence on the THz modulation depth, we examined the pump fluence-dependent OPTP responses of the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 and Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 , as shown in Figure 4a,d, respectively.

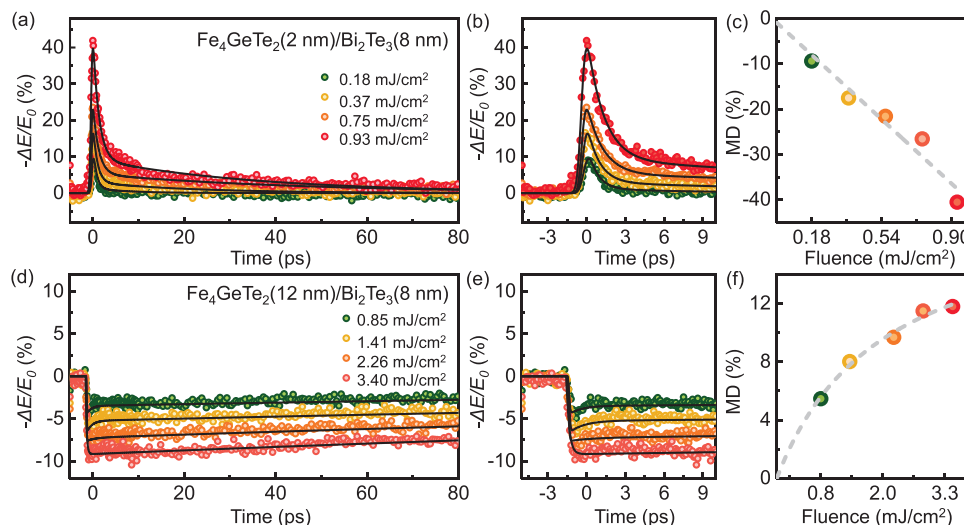


Figure 4. OPTP measurements of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures at different pump fluences at room temperature. a) Pump fluence-dependent OPTP dynamics for the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm). b) Initial time windows of the OPTP signals are shown in (a). c) The modulation depth (MD) of Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) as a function of pump fluence. d) Pump fluence-dependent OPTP dynamics for the Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 (8 nm). e) Initial time windows of the OPTP signals are shown in (d). f) The MD of Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 (8 nm) as a function of pump fluence.

Figure 4b,e exhibit the initial time windows of the OPTP signals in Figure 4a,d, respectively. For the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 , the value of MD is negative and decreases linearly with pump fluence, ranging from -9.4% at 0.18 mJ cm^{-2} to -42.2% at 0.93 mJ cm^{-2} , as shown in Figure 4c. This observation is consistent with the increased density of mobile charge carriers following photoexcitation. All experimental data are fitted by the double-exponential decay function, as shown in the black curves in Figure 4a. The extracted fitting parameters are summarized in Note S6 (Supporting Information). Both the fast and slow relaxation times increase with the pump fluence, which may be attributed to the hot phonon bottleneck effects at the surface state of Bi_2Te_3 . As the pump fluence increases, the occupancy rate of phonons becomes large enough, and thus the coupling between carriers and phonons will be weakened. This leads to prolonged relaxation times. In contrast, for the Fe_4GeTe_2 (12 nm)/ Bi_2Te_3 , the THz conductivity decreases after illumination, following a two-step relaxation process. As shown in Figure 4f, the value of MD is positive and increases from $+5.5\%$ at 0.85 mJ cm^{-2} to $+10.8\%$ at 3.4 mJ cm^{-2} , and starts to saturate. As highlighted in Figure 4e, we observed a fast relaxation process at low pump fluence, indicative of a fast electron-phonon coupling. The fast relaxation component becomes less observable at higher pump fluence. While the slow relaxation process on the order of hundreds of picoseconds can be related to the slow bottleneck decay of the electrons due to the low thermal conductivity.

Finally, to gain a deeper understanding of how the topological surface electrons participate in the modulation of THz waves, we further investigated the influence of temperature on the OPTP data in the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure. Figure 5a shows the transient THz transmission at various temperatures for a fixed pump fluence of 0.5 mJ cm^{-2} . No external magnetic field has been applied to the sample. It is found that the photocarrier dynamics is strongly temperature-dependent. At room temperature, $-\Delta E/E_0(\Delta t)$ increases as the

pump pulse arrives at the sample, which can be well-explained by increases in the number of free carriers. However, below 40 K, $-\Delta E/E_0(\Delta t)$ exhibits a short-lived positive photoconductivity followed by a slow evolution to its negative maximum value of $\approx 20 \text{ ps}$. Figure 5b highlights the initial short-time window of the OPTP traces. Figure 5c plots the values of $-\Delta E/E_0$ collected at peak position and $\Delta t = 0, 1, 5, 10, 20 \text{ ps}$ as functions of temperature. We find that the peak signal of PPC (green circles) increases monotonously with decreasing temperature. While, the $-\Delta E/E_0$ signals collected at $\Delta t = 0, 1, 5, 10$, and 20 ps , remain nearly constant decreasing from 300 K to 120 K. Below 120 K, they exhibit a rapid decrease in photoconductivity behavior. Different temperature dependents indicate their different physical mechanism.

To understand the short-lived positive photoconductivity, we compare the $-\Delta E/E_0(\Delta t)$ in the absence of an external magnetic field with that measured under an applied magnetic field of $\pm 0.5 \text{ T}$, as shown in Figure 5d. It can be found that the magnetic field dependent THz emission from the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures overlaps with the short-lived positive response of $-\Delta E/E_0(\Delta t)$ in terms of time. Therefore, the enhanced peak signal of PPC at lower temperatures can be attributed to the increased THz emission resulting from the enhanced spontaneous magnetization, consistent with reference.^[71]

It can be found that the value of $-\Delta E/E_0$ collected at $\Delta t = 20 \text{ ps}$ transitions from positive to negative as the temperature decreases below 120 K. The transition time from PPC to NPC is $\approx 20 \text{ ps}$. This process cannot be attributed to the dynamical formation of polarons, as the time constant for polaronic formation typically occurs on the order of 400 fs in several materials, including polar lead iodide perovskites,^[57,72] Dirac semimetals^[55,73] and thermoelectric materials.^[74] Therefore, the contribution of polaron formation to the NPC can be ruled out. Actually, the appearance of the NPC signal at low temperatures has also been observed in topological crystalline insulator PbSnSe .^[70] At moderate temperatures, the transition from PPC to NPC can be explained by the

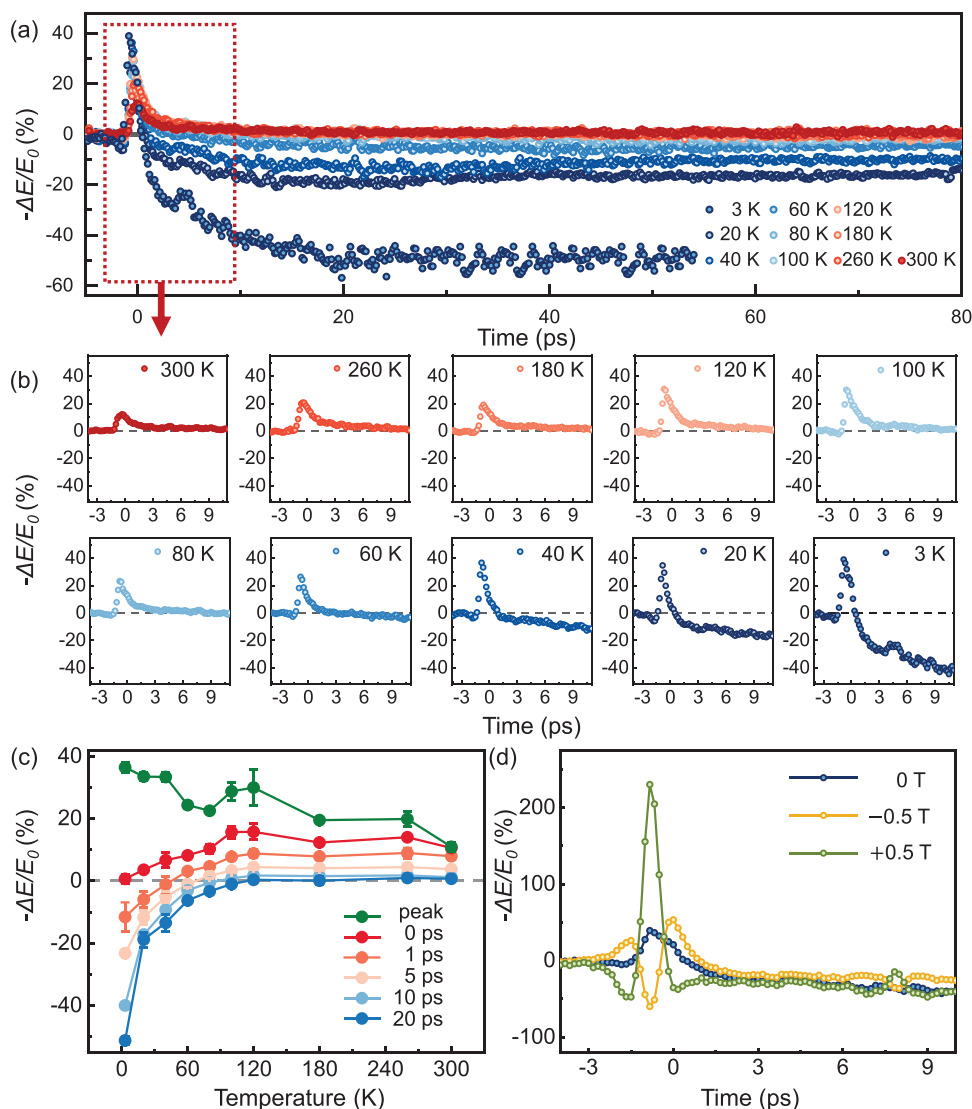


Figure 5. OPTP measurements of Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure at different temperatures. a) Pump-probe traces at different temperatures for the Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure. b) Highlights of the temporal behaviors in a short-time window, in the temperature range from 300 to 3 K. c) Temperature dependence of pump-probe traces measured at peak positions and fixed probe delays of $\Delta t = 0, 1, 5, 10$, and 20 ps. d) Comparison of $-\Delta E/E_0$ (Δt) for Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure at 3 K, measured with $\pm H$ and without H .

coexistence and competition of Dirac fermions from the surface states and massive fermions from the bulk states in Bi_2Te_3 . The strength of $-\Delta E/E_0$ collected at $\Delta t = 20$ ps decreases as the temperature is lowered, which means the effect of the Dirac fermions is enhanced at low temperatures.

It is noteworthy to comment that the sign reversal of THz photoconductivity has been established by controlling (1) the contributions of carrier accumulation effect and thermal effect, as observed by the thickness-dependent experimental results, and (2) the contributions of Dirac fermions from the surface states and massive fermions from the bulk states, as investigated by the temperature-dependent experimental results. The switchability between the THz NPC and PPC states can be denoted as “+1” and “−1” states, respectively. This capability enables non-ambiguous states, which can facilitate photo-modulation applica-

tions, such as low-power photodetection, opto-logic gates multi-bit memory devices, etc. A proof-of-concept approach is presented based on the observed sign reversal of THz photoconductivity in $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures.

3. Conclusion

To summarize, we have employed ultrafast OPTP spectroscopy to investigate the generation and relaxation dynamics of photoconductivity in 2D all-vdW ferromagnet/topological insulator heterostructures. Based on the thickness-dependent experimental results, the significant features of the transient THz transmission are attributed to hot carrier accumulation and thermal effects. For a Fe_4GeTe_2 (2 nm)/ Bi_2Te_3 (8 nm) heterostructure, we observe a transition from positive to negative photoinduced

conductivity with decreasing temperature, which is a result of the increased surface state Dirac fermions at low temperatures. Our present findings provide critical details for potential applications of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures for all-optical control THz ultrafast modulation and THz logic and signal processing applications.

4. Experimental Section

Fabrication of $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ Heterostructures: Fe_4GeTe_2 , Bi_2Te_3 thin films, and their heterostructures were grown on Al_2O_3 substrates (500 μm) using MBE under a base vacuum of 10^{-10} Torr. After pre-annealing of the substrate at 600 $^\circ\text{C}$, the Fe_4GeTe_2 film was grown by evaporating high-purity Fe, Ge, and Te from standard Knudsen effusion cells with a controllable flux ratio. While Bi_2Te_3 thin film was deposited on the substrate with a Bi and Te flux ration of 1:15. High-quality Fe_4GeTe_2 (2, 6, 10, 12 nm)/ Bi_2Te_3 (8 nm) and Fe_4GeTe_2 (4 nm)/ Bi_2Te_3 (3, 6, 8, 12 nm) heterostructures were grown following the above growth condition with the growth sequence of Bi_2Te_3 first and Fe_4GeTe_2 later. Finally, a 2 nm thick Ge layer was grown on the Fe_4GeTe_2 films as a protective layer to prevent environmental degradation and damage during subsequent processing.

THz Time-Domain Spectroscopy (THz-TDS): Broadband THz-TDS was carried out on the $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures with the PCA-scanner system. A femtosecond laser pulse (70 mW, 100 fs duration, 1550 nm wavelength, 100 MHz repetition rate) was split into two beams: generation and detection laser beams. The generated laser beam has a power of 27.5 mW, whereas the detection laser beam has a power of 21.2 mW. The generated laser beam was focused onto a 100 μm InGaAs antenna as the emitter. The generated THz beam was focused by a parabolic mirror and transmitted through $\text{Fe}_4\text{GeTe}_2/\text{Bi}_2\text{Te}_3$ heterostructures. The amplitude and phase of the transmitted THz pulses were detected by another InGaAs photoconductive switching, by scanning a variable optical delay stage. All static THz spectra were obtained at a room temperature with a dry air environment.

Optical Pump-Terahertz Probe Spectroscopy: The optical pump-terahertz probe Spectroscopy (OPTP) system was conducted in a transmission geometry. The system utilized a Ti:sapphire laser (Mira 900 and Legend Elite Duo, Coherent Inc.) to generate laser pulses with a central wavelength of 800 nm, a repetition rate of 1 kHz, and a pulse duration of 120 fs. The laser beam was split into three paths: the THz generation beam, the THz probe beam, and the optical pump beam. The THz generation beam was directed to excite the (110) ZnTe crystal (1 mm thick) producing THz waves. These THz waves were subsequently aligned and focused onto the sample using a pair of off-axis parabolic mirrors. After interacting with the sample, the THz waves were refocused onto the detection system using another pair of off-axis parabolic mirrors. The THz detection was performed using electro-optic sampling based on the Pockels effect. Both the THz probe beam and the THz waves were co-focused onto the ZnTe crystal (1 mm thick) used for detection. A quarter-wave plate was placed after the electro-optic crystal to convert the THz probe beam passing through the crystal into circularly polarized light. Finally, the probe beam was split into s-polarized and p-polarized components using a

Wollaston prism, and the polarization changes were measured using a balanced photodiode. For the low-temperature OPTP experiment, the sample was placed inside a temperature-variable chamber (TeslatronPT, Oxford Instruments) located between parabolic mirrors and cooled to ≈ 3 K.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dirac fermions, optical-pump terahertz-probe spectroscopy, ultrafast terahertz conductivity dynamics, van der waals ferromagnet/topological insulator heterostructures

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