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Ultrafast Spin-To-Charge Conversion at the Surface of Topological Insulator Thin Films

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Topological insulators (TIs) provide a fascinating counterexample where strong spin-orbit interaction leads to the formation of spin-momentum-locked (topological) surface states,^[1,2] and are anticipated to mediate superior spin-charge conversion (SCC).^[3,4] As a result, employing conventional steady-state transport set-ups, TIs have been exploited to switch the magnetization direction of adjacent ferromagnetic (FM) layers,^[5-12] as well as generate charge current from spin current.^[13-18] However, these transport studies involved contact fabrication, required complicated data analysis to extract the spin-related component, and whose signal

are in the DC regime. Direct access to the *dynamics* of SCC – a crucial ingredient in optimizing TI based spintronic devices – remains conspicuously missing. The difficulty of tracking SCC dynamics stems from the need to address both the ultrafast timescales involved as well as obtain spin resolution simultaneously.

In this work, we directly probe the dynamical processes of SCC in $\text{Bi}_2\text{Se}_3/\text{Co}$ heterostructures for the first time, via ultrafast spin injection and terahertz (THz) emission spectroscopy. Ultrafast spin injection from ferromagnetic Co enables transient spin currents to be injected.^[19-22] At the same time, given the challenging timescales involved, THz emission spectroscopy – the central signature we track — is a powerful optical tool, which offers a contact-free amperemeter with sub-picosecond resolution. As we describe below, this technique combined with a systematic exhaustion of the experimental parameters of the $\text{Bi}_2\text{Se}_3/\text{Co}$ heterostructure and our ultrafast setup (thickness, temperature, Co magnetization direction, optical pulse polarization, etc.), enables an unprecedented detailed window into the key parameters of SCC including the timescale as well as the spatial locality of ultrafast spin-to-charge conversion.

In particular, we find a highly efficient THz emission (mediated by ultrafast spin injection) from the $\text{Bi}_2\text{Se}_3/\text{Co}$ heterostructure. Strikingly, this far outstrips (up to an order of magnitude) the emission of either bare Bi_2Se_3 or Co films taken individually, indicating the highly efficient SCC in the $\text{Bi}_2\text{Se}_3/\text{Co}$ stack, as well as the central role SCC plays in the optical response of the heterostructure. Crucially, the THz signal in the $\text{Bi}_2\text{Se}_3/\text{Co}$ stack exhibits a significant enhancement when the thickness of Bi_2Se_3 increases from four to six quintuple layers. Coinciding with the appearance of well-defined surface states,^[23] this indicates the dominant role of surface states in the SCC processes.

In addition, varying pump polarization enables a direct tracking of the SCC process. We identify the fundamental timescale for ultrafast SCC formation in $\text{Bi}_2\text{Se}_3/\text{Co}$ to be ~ 0.12 ps. This sets a characteristic cut-off time for SCC processes in TI spintronic heterostructures. Our

results provide fundamental insights into the ultrafast SCC processes and indicate the central role of topological surface states in the very efficient SCC at room temperature for THz opto-spintronic applications.

Dynamical response of pure Bi₂Se₃ thin films. In order to methodically delineate the THz emission signals in our Bi₂Se₃/Co heterostructures (see below), we first describe the optical response (focusing on its THz response) of pure Bi₂Se₃ thin films grown by molecular beam epitaxy (MBE). As we will discuss, this enables us to clearly isolate the new dynamics that arises due to the TI/FM heterostructure stack from the response of either the pure TI or pure FM by themselves.

Bi₂Se₃ thin films samples were setup in a transmission geometry, as shown in **Figure 1a**, where an 800-nm pump beam with 60 mW power impinged on the samples at normal incidence, and only the vertical components of the emitted THz pulses were detected by electro-optic sampling. The typical THz electric field waveforms emitted from Bi₂Se₃ films are plotted in Figure 1b. The spectra of the detected THz signals, as shown in the inset of Figure 1b, covers the frequency range up to 3 THz, which is limited by the electro-optic detection of 1-mm-thick ZnTe crystal. A SiO₂ capping layer is essential to protect the Bi₂Se₃ film from the atmosphere, and prevent the evaporation of the thin film under pulsed-laser illumination due to weak van der Waals type coupling between two neighbor quintuple layers (QLs, 1 QL~1 nm).^[24] The detected THz traces show a distinct dependence on the pump polarization. Figure 1c shows the THz peak amplitude as a function of pump polarization angle, which could be well fitted by a sinusoidal function with a period of 180°. In addition, the dependence of THz amplitude on sample azimuthal angle reveals a characteristic three-fold symmetry (see Figure S1), which is associated with the crystalline symmetry of Bi₂Se₃.^[25] These are in good agreement with the expectations from the shift current mechanism (see the Supporting Information, Section S1, for further exclusion of other mechanisms).^[26] Additionally, we note that the dependence of THz peak amplitude on the

incident pump power, as indicated in the inset of Figure 1d, shows a nonlinear behavior, which we attribute to saturable absorption (see the Supporting Information, Section S2).^[27]

In principle, the shift current is a second-order nonlinear effect, which requires the breaking of spatial inversion symmetry,^[28] and hence can only be excited on the surface of three-dimensional TIs.^[25] Consequently, the amplitude should be independent of the thickness of Bi₂Se₃ film. Indeed, the THz peak amplitude is roughly constant for the samples above 6 QL, as illustrated in Figure 1d. Interestingly, for the 4-QL sample, the measured THz signal is about one order of magnitude smaller than that from the films above 6 QL. It has been reported that the shift current in Bi₂Se₃ originates from the transient charge transfer along the Se-Bi bonds involving the surface-states-related optical transitions.^[26] However, for the ultrathin Bi₂Se₃ film with a thickness below 6 QL, the coupling between the top and bottom surface opens a gap in the surface-state dispersion,^[23] and hence suppresses the surface-states-related optical transitions.^[29] Therefore, the shift current and resulting THz emission decrease considerably. This observation indicates that the THz emission from pure Bi₂Se₃ film is a surface-dominated response.

Giant THz emission from Bi₂Se₃/Co heterostructures. We now turn to investigate the THz response of Bi₂Se₃/Co heterostructures. As we show below, the dynamics of this TI/FM heterostructure starkly contrasts with that of the TI by itself. The experiments are performed under identical conditions as that for the pure Bi₂Se₃ films, except that an in-plane external static magnetic field ~800 Oe is applied to orient the Co magnetization, as sketched in **Figure 2a**. The THz waveform emitted from Bi₂Se₃/Co heterostructure, together with that from pure Bi₂Se₃ and Co films, are shown in Figure 2b.

Strikingly, the THz emission from the heterostructure is significantly enhanced after the deposition of a Co layer. Indeed, for the same TI film thickness, the THz emission amplitude from the Bi₂Se₃/Co heterostructure (orange curve) is about an order of magnitude larger than that of pure Bi₂Se₃ film by itself (blue curve). We note that the detected THz emission from a

3-nm Co film by itself (green curve) is weak; this indicates that the laser-induced demagnetization in the magnetic film contributes negligibly to THz emission in TI/FM heterostructure.^[30,31] Furthermore, in contrast to that of the pure Bi₂Se₃ film, the THz emission amplitude from the heterostructure obeys a linear power dependence up to high power (> 40 mW), as illustrated in the inset of Figure 2d. These observations indicate that THz emission from the heterostructure cannot be explained by dynamics from that of the pure TI or FM by themselves.

Instead, as we now explain, it arises from the novel coupled spin-charge dynamics in the Bi₂Se₃/Co heterostructure. In order to understand this, we note that under the illumination of 800 nm laser beam, a spin-polarized current is set up at the interface of Bi₂Se₃/Co heterostructure due to the different mobilities of the majority- and minority-spin *sp*-band electrons in the Co layer.^[19] Due to the existence of strong SOC in Bi₂Se₃, the ultrafast injected spin current can be converted to an ultrafast charge current via either inverse Edelstein effect (IEE) on the surface or inverse spin Hall effect (ISHE) in the bulk.^[32-35] This SCC conversion process can lead to the large-amplitude THz waveforms that we detect from the TI/FM heterostructure. We note that the SCC transient charge currents generated by both IEE and ISHE flow in the same direction — since $\mathbf{j}_c \propto \hat{\mathbf{z}} \times \boldsymbol{\sigma}$ in IEE^[13,34,36] and $\mathbf{j}_c \propto \mathbf{j}_s \times \boldsymbol{\sigma}$ in ISHE,^[32,35] where $\mathbf{j}_c$ is the charge current, $\mathbf{j}_s$ is the spin current, $\boldsymbol{\sigma}$ is the direction of the spin polarization, and $\hat{\mathbf{z}}$ is the unit vector normal to the TI/FM interface (which is parallel to $\mathbf{j}_s$). As a result, the polarization of the emitted THz pulses from both ISHE and IEE also point in the same direction.

To confirm the central role of SCC in the Bi₂Se₃/Co stack THz emission, we oriented the magnetization in the Co layer using an in-plane magnetic field — this enables the tuning of the spin-polarization injected into the TI film. As shown in Figure 2c, the polarity of the emitted THz pulses reverses when either (1) the direction of magnetic field was reversed, or

when (2) the pump beam was incident on the opposite side of the heterostructure, as expected from SCC (IEE and/or ISHE) THz emission mechanism. While (1) displays the spin origin of the Bi₂Se₃/Co stack THz emission, (2) displays its spin-current dependence, since the spin current flips its direction relative to the lab frame when the sample is pumped from the back.

Indeed, since the spin polarization σ is determined by the external magnetic field, the abovementioned two SCC mechanisms also predict that the measured (x -projected) THz electric field, obeys $E_{THz}^x \propto |\mathbf{j}_s \times \sigma|_x \propto \sin\phi$, where ϕ is the magnetic field angle with respect to the positive x -axis. As shown in Figure 2d, the THz peak amplitude is locked to the magnetic field direction and exhibits a one-fold sinusoidal behavior, and allows direct magnetic field control of THz emission. We therefore demonstrated a novel spin-charge dynamics that is enabled by SCC in TI/FM heterostructures.

Separation of THz waveforms and SCC timescale. Pump-polarization-dependent measurements provide a further means of quantifying the contributions to the THz emission from the Bi₂Se₃/Co heterostructures. In contrast to that from pure Bi₂Se₃ films, we observe only small changes in the amplitude and phase of the measured THz waveform as a function of pump polarization angle, as shown in **Figure 3a**. This is fully consistent with a dominant THz emission contribution from SCC that is independent of pump polarization.^[20-22] Figure 3b plots the THz electric field at $t = 0$ ps, as a function of pump polarization angle, showing a small-amplitude oscillation superposed on top of a large dc offset. As explained in the last section, the small-amplitude polarization-dependent contribution can be ascribed to the THz generation from the Bi₂Se₃ film itself.

On the basis of these characteristics, we can separate out the THz waveform contributed by (a) the TI film alone (that is via the shift-current mechanism), $E_{TI}(t)$, and (b) from SCC in the TI/FM heterostructure, $E_{SCC}(t)$. This is done by performing for (a) $E_{TI}(t) = [E(t, \theta = 0^\circ) - E(t, \theta = 90^\circ)]/2$, and for (b) $E_{SCC}(t) = [E(t, \theta = 0^\circ) + E(t, \theta = 90^\circ)]/2$. The resulting

delineated THz waveforms are shown in Figure 3c. For sake of comparison, the THz waveform emitted from pure 10-QL Bi_2Se_3 film is also plotted. Notice that in the Co/ Bi_2Se_3 heterostructure, the THz signal contributed by the shift-current mechanism is smaller than that from pure Bi_2Se_3 — this can be attributed to the reflection or absorption of the 800-nm pump beam by the Co film. The extracted TI component shows a very similar temperature dependence to that of pure Bi_2Se_3 film, as shown in Figure S6, giving further evidence that they share the same origin (see the Supporting Information, Section S6).

Interestingly, this delineation enables a temporal difference between these two extracted THz waveforms to be discerned — the SCC-component lags the TI-component (shift current) by ~ 0.12 ps. This can be seen more clearly in the plot of normalized THz waveforms in the inset of Figure 3c.

The significance of this delay can be appreciated by first noting, that to a good approximation, we can assume that the 800-nm light hits the surface of Co and Bi_2Se_3 layer simultaneously due to the ultrathin Co layer. Upon optical excitation, the shift current originates from the instantaneous shift of electron density along the Se-Bi bond,^[26] while it takes a longer time to generate a spin current in FM layer, diffuse into the Bi_2Se_3 film, and then be converted to a charge current.^[20,22] To quantify the spin transport in the FM layer, we vary the Co thickness from 2 to 16 nm while keeping the thickness of Bi_2Se_3 fixed at 10 QL. The amplitude of the THz signal contributed by SCC component is maximum at ~ 3 nm, and then decreases with increasing Co thickness (see Figure S2), which we attribute to the smaller amounts of 800-nm light reaching the Co/ Bi_2Se_3 interface due to absorption of 800-nm light by Co^[37] and hence smaller injection of the laser-driven spin current.^[20,22] Figure 3d shows that the extracted temporal delay is independent of the thickness of Co layer. This is consistent with the picture of superdiffusive spin transport in Co, where the timescale of the multiplication of carriers is only dependent on the material (see the Supporting Information, Section S3). Therefore, the temporal difference of ~ 0.12 ps corresponds to the time needed

for the formation of a maximum charge current from the peak of the laser pulse, and thus characterizes the SCC processes in the Bi₂Se₃/Co heterostructure. This value is in the same order as that deduced by theoretical simulations of the spin dynamics (0.1 – 0.3 ps) in heavy-metal/FM heterostructures.^[20,22]

Thickness dependence of THz emission from Bi₂Se₃/Co heterostructures. In order to verify whether the observed SCC is dominated by IEE on the surface or ISHE in the bulk, we perform measurements on different thicknesses of Bi₂Se₃ film while fixing the Co thickness at 4 nm. **Figure 4a** shows the THz peak amplitude of the extracted SCC component as a function of Bi₂Se₃ thickness. At 4 QL, the emitted THz signal is relatively small, while it increases by about one order of magnitude as we go from 4 to 6 QL. We see the same thickness dependence of THz emission in pure Bi₂Se₃ films with thicknesses from 4 to 10 QL (shown in Figure 1d), indicating therefore that the THz emission mechanism in TI/FM is also a surface-dominated response. The dramatic enhancement of THz signal at 6 QL can be ascribed to the formation of gapless surface states,^[23] as has been discussed earlier in pure Bi₂Se₃ films.

On the other hand, if ISHE in the bulk were to play a major role in THz emission of TI/FM heterostructures, the detected THz signal can be written as $E_{THz}^x \propto \lambda_{sf} \tanh(d/2\lambda_{sf})$, where λ_{sf} is the spin diffusion length and d is the thickness of Bi₂Se₃ film.^[18,33,38] However, this spin diffusion model cannot account for the Bi₂Se₃ thickness dependence of THz peak amplitude (see the Supporting information, Section S4). Therefore, we conclude that the SCC processes in TI/FM heterostructures are dominated by the topological surface states, though we cannot completely exclude a possible contribution from ISHE in the bulk. For the thicker samples (above 10 QL), the extracted THz signal decreases with increasing thickness. This probably originates from the carrier absorption in the bulk since the THz transients are generated at the interface of the heterostructure. Figure 4a also shows the electric-field

transmittance of pure Bi_2Se_3 films at 1 THz (corresponding to the peak of THz waveforms) upon optical excitation, which decreases with increasing film thickness (see the Supporting Information, Section S5). The observed agreement between the thickness dependence of THz signal and pump transmittance (for samples above 4 QL) suggests that the suppression of THz amplitude is attributed to the absorption of THz radiation by both the intrinsic bulk carriers and the photo-generated free carriers in Bi_2Se_3 films.

Temperature dependence. We also investigate the temperature dependence of THz emission from both the Bi_2Se_3 (10 QL) film and the $\text{Bi}_2\text{Se}_3/\text{Co}$ (4 nm) heterostructures with different Bi_2Se_3 thicknesses. Cooling the pure Bi_2Se_3 film from room temperature down to 10 K increases the emitted THz signal, which we attribute to a higher carrier mobility at low temperature (see the Supporting Information, Section S6). In contrast, as shown in Figure 4b, the THz peak amplitude of the extracted SCC component does not change with temperature for four representative samples with different Bi_2Se_3 thicknesses. In this temperature range (10 – 300 K), the spin diffusion length of the Co layer (38 – 59 nm) is much larger than the thickness of Co layer used in our case,^[39] implying a constant spin current injection from the Co layer into the TI at different temperatures. Therefore, the temperature-insensitive THz emission implies that the SCC efficiency via IEE is also independent of temperature. This is consistent with previous work on the temperature evolution of IEE in metallic Ag/Bi junction.^[40] In TIs, IEE originates from the spin-momentum-locked surface states, which is a result of strong SOC.^[1,2] As a relativistic effect, it is expected to be temperature-independent.^[41] Consequently, the resulting THz signal contributed by the IEE should be temperature insensitive, in good agreement with our experimental results, confirming once again the dominant contribution from the topological surface states to the observed SCC in TI/FM heterostructures.

The spin-momentum-locked topological surface states have been predicted to possess superior SCC efficiency.^[1,3,4] However, previous reported values of the SCC efficiency

exhibit a large range over several orders of magnitude (from 10^{-4} to 0.8).^[13-17] In order to evaluate the SCC efficiency in Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure, we compare its THz emission amplitude to that from the Pt (2 nm)/Co (3 nm) bilayer structure — we choose a Pt thickness of 2 nm to match a single TI surface state thickness of ~ 2 nm,^[42,43] since SCC via IEE is restricted to the top surface of Bi_2Se_3 in the heterostructure. As shown in Figure S7, the THz peak amplitude of Bi_2Se_3 (10 QL)/Co (3 nm) is ~ 1.7 times of that from Pt (2 nm)/Co (3 nm) under identical experimental conditions. Since the injected spin currents for both heterostructures are driven from the Co layer into the heavy metal (Pt) or TI (Bi_2Se_3) by the same mechanism, the injected spin currents have similar magnitudes in both heterostructures (see the Supporting Information, Section S7).^[19,20] Consequently, the effective SCC efficiency $\theta_{eff} = j_c/j_s$ is a function only of charge current and hence THz signal amplitude. As a well-studied heavy metal with large SOC, the SCC efficiency of a 2-nm thick Pt film was determined to be ~ 0.03 .^[44] Thus, we estimate $\theta_{eff} \sim 0.03 \times 1.7 \approx 0.05$ for 10-QL Bi_2Se_3 film — this is within the range of previously-reported values.^[14,15] Also, as has been discussed earlier, the effective film thickness t , which contributes to the SCC, is the surface state thickness of ~ 2 nm.^[42,43] From this value of $t \sim 2$ nm and the deduced $\theta_{eff} \sim 0.05$ for Bi_2Se_3 , we can estimate the IEE length $\lambda_{IEE} = \frac{1}{2} \theta_{eff} t \sim 50$ pm (see the Supporting Information, Section S4). This IEE length is a measure of SCC efficiency for surfaces or interfaces,^[33,45] and its value is comparable to that derived from spin-pumping measurements in TI/ferromagnetic-insulator heterostructures (35–76 pm).^[18,46] Remarkably, the amplitude of THz emission from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure is only slightly smaller than that from the Pt (6 nm)/Co (3 nm) bilayer structure (see Figure S7), and the latter has been demonstrated to be a very efficient broadband THz emitter comparable to the standard ZnTe THz emitter.^[21,22,47] In this regard, the temperature-insensitive SCC efficiency suggests

promising applications of topological surface states in THz spintronic devices at room temperature.

In conclusion, we have systematically demonstrated, for the first time, highly-efficient ultrafast spin-injection and spin-to-charge conversion in topological-insulator/ferromagnet heterostructures using THz emission spectroscopy. Locked to the Co magnetization direction, THz emission from Bi₂Se₃/Co heterostructures far outstrips the emission of either Bi₂Se₃ or Co individually. This underscores the central role the novel TI spin-charge dynamics play in response of the heterostructure. While we have focused on the THz response of Bi₂Se₃/Co to elucidate its SCC dynamics, large non-equilibrium spin injection into a TI afforded by our methodology unlocks easy access to a range of spin-type responses previously difficult to realize in TIs, including tunable generation of ultrafast spin and charge current in the bulk and/or surface. Perhaps most tantalizing is the fast timescale in which efficient SCC in Bi₂Se₃ occurs within ~0.12 ps. This paves the way for high speed and ultra-thin opto-spintronic devices with operating speeds up to several terahertz.

Experimental Section

Sample fabrication: High-quality thin films of topological insulator Bi₂Se₃ with different thicknesses of 4, 6, 8, 10, 20, and 40 QLs were grown by two-step deposition process using MBE technique on 0.5 mm thick c-axis Al₂O₃ substrate. The samples were transferred through air into the sputtering chamber for capping layer and magnetic layer deposition. For pure Bi₂Se₃ films, the samples were protected by a 4-nm-thick SiO₂ capping layer. For the Bi₂Se₃/Co heterostructures, nanometer-thick Co layer (2 to 16 nm) was deposited on the Bi₂Se₃ films by sputtering and then capped by the same capping layer to prevent oxidation of the magnetic layer. For comparison, a pure Co layer (3 nm) on an Al₂O₃ substrate with the same capping layer was also prepared.

THz emission setup. A Ti:sapphire regenerative amplifier (Coherence Legend; center wavelength 800 nm; duration 50 fs; repetition rate 1 kHz) was employed in this work. The beam was split into two parts: one for pump beam and the other one for THz detection, by an optical beam splitter. The pump beam with an incident power of 60 mW and a spot size ~ 7 mm impinged on the samples at normal incidence from the sample side. Any residual pump beam after the sample was blocked by a piece of 1/16-inch-thick high-density polyethylene (HDPE), which is transparent in THz frequency range. The generated THz pulses were projected onto x-axis (vertical) by using a wire-grid THz polarizer, and then collected and focused by two parabolic mirrors onto a 1-mm-thick $\langle 110 \rangle$ ZnTe crystal for free-space electro-optic sampling. A cryostat was used in the temperature-dependent experiments, in which the magnets were fixed along the y (horizontal) direction. The remaining experiments were performed at room temperature in a dry air atmosphere. A half-wave plate and a pair of permanent magnets in dipole configuration were mounted on rotation stages to vary the polarization of pump pulses and to align the magnetization of Co layer, respectively. A visible wire grid polarizer for the 800-nm beam was placed before the half-wave plate. The magnetic field at the sample position was ~ 800 Oe.

Supporting Information

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

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Figure 1. THz emission from Bi₂Se₃ thin films. (a) Schematic illustration of THz emission from Bi₂Se₃ films. The sample is excited by femtosecond laser pulses (800 nm, 60 mW) from the sample side, and vertical component of the emitted THz pulses is detected by electro-optic sampling. θ is polarization angle of pump beam with respect to the x -axis. (b) Typical THz waveforms emitted from Bi₂Se₃ films with different thicknesses. The inset shows the corresponding spectra. (c) Peak amplitude of THz waveforms from 10-QL Bi₂Se₃ film as a function of polarization angle θ . The solid line shows a sinusoidal fit. (d) The peak amplitude of THz signal as a function of Bi₂Se₃ thickness. The dash line is a guide to the eye. The inset shows the power dependence of THz emission from 10-QL Bi₂Se₃ film, exhibiting a saturation behavior. The solid line shows the fit with the saturable absorption model.

Figure 2. THz emission from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure. (a) A sketch of the experimental geometry for Bi_2Se_3 /Co heterostructure. An external magnetic field H_{ext} is applied to align the Co magnetization. (b) THz waveforms generated from Co (3 nm) film, Bi_2Se_3 (10 QL) film, and Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure. (c) THz waveforms emitted from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure measured with front and back sample excitation and reversed magnetic field. Note that the differences in amplitude and time delay of THz waveforms on pumping the samples from opposite sides originate from the different refractive indices of the sapphire substrate in the 800-nm and THz frequency range. (d) The peak amplitude of THz pulses emitted from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure as a function of magnetic field angle ϕ . The solid line shows a sinusoidal fit. Inset: Power dependence of THz emission from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure. The solid line shows a fit with saturable absorption model. The dash line shows a linear fit to the data below 40 mW.

Figure 3. Separation of THz waveforms and SCC timescale. (a) THz waveforms generated from Bi_2Se_3 /Co heterostructure under various pump polarization. Inset: Enlarge of the THz waveforms near the peak. (b) The electric field of THz traces at $t = 0$ ps as a function of pump polarization angle θ . The solid line shows a sinusoidal fit with a large offset as indicated by the dashed line. (c) The extracted THz waveforms contributed by the SCC and TI components. The THz signal from pure Bi_2Se_3 (10 QL) film is also shown for comparison. The inset shows the normalized waveforms. (d) The extracted temporal delay between the SCC and TI components as a function of Co thickness. The dash line is a guide to the eye.

Figure 4. Bi₂Se₃ thickness and temperature dependence of THz emission. (a) THz peak amplitude of the extracted SCC component from Bi₂Se₃/Co (4 nm) heterostructures (red) and THz electric field transmittance amplitude of Bi₂Se₃ films under a pump power of 30 mW (blue), as a function of Bi₂Se₃ thickness. (b) Temperature dependence of the THz peak amplitude of the extracted SCC component from Bi₂Se₃/Co (4 nm) heterostructures with different Bi₂Se₃ thicknesses.

Supporting Information

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Ultrafast Spin-To-Charge Conversion at the Surface of Topological Insulator Thin Films

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Section S1: Shift-current mechanism in Bi₂Se₃ films.

Several basic mechanisms of THz radiation from semiconductors, including the photo-Dember effect,^[1,2] surface-depletion field effect^[2-4] and nonlinear optical processes,^[3-6] have been employed to explain THz emission from topological insulators. However, both the photo-Dember effect and surface-depletion field effect are associated with the surge current flowing along the surface-normal direction and hence emitting THz radiations along the sample plane. They are not responsible for THz generation at normal incidence because only the THz component propagating in the z direction was detected in the present study. In the case of high-intensity excitation, the nonlinear optical processes, such as optical rectification and photogalvanic effect (PGE), become dominant. These second-order effects require the breaking of spatial inversion symmetry and hence can be excited only on the surfaces of three-dimensional topological insulators.^[7] THz radiation via optical rectification has its physical origin in the transient dielectric polarization that roughly follows the intensity envelop of pump pulse. It is governed by the second-order susceptibility coefficient of the crystal, and thus should be independent of the thickness of sample. Certainly, the 6 QL Bi₂Se₃ film leads to a strong THz radiation (Figure 1d in the main text), while, for the 4 QL Bi₂Se₃ sample consisting of only two surface layers, THz signal is one order of magnitude smaller. Therefore, we can exclude the possible contribution of optical rectification in our

configuration. In principle, the circular PGE is induced by circularly polarized light and would vanish at normal incidence.^[8,9] In the present study, application of linear polarized pump beam leads to the linear PGE on the surfaces of Bi₂Se₃, which is also referred to the shift current.^[5]

Figure S1. Symmetry of THz emission from Bi₂Se₃ film. The left bottom panel is the amplitude mapping of THz radiation emitted from Bi₂Se₃ (10 QL) films as a function of sample azimuthal angle α and pump polarization angle θ . Sample azimuthal angle α characterizes the rotation angle of the sample about its surface normal. The left top and right bottom panels show the cuts along the white lines as indicated in the main panel. The solid line shows a nice fit to sine function. The right top figure shows a simulation to the THz peak amplitude with the function of $\sin(2\theta - 3\alpha)$.

The THz electric field amplitude dependence on the polarization angle shows a characteristic two-fold symmetry, and exhibits three-fold symmetry on the azimuthal angle as illustrated in Figure S1. It has been shown that the polarization dependence of the linear PGE current excited at normal incidence can be presented as:^[7,9]

$$j_x = \chi |E_0|^2 \sin(2\theta - 3\alpha)$$

$$j_y = -\chi |E_0|^2 \cos(2\theta - 3\alpha)$$

where the χ is the independent nonzero component of second-order susceptibility tensor, E_0 is the electric field strength of pump beam, θ and α represent the pump polarization angle and

sample azimuthal angle, respectively. According to the Maxwell's equations, the THz electric field amplitude is proportional to the first-time derivative of the transient current. Consequently,

$$E_{THz}^x \propto \sin(2\theta - 3\alpha)$$

$$E_{THz}^y \propto \cos(2\theta - 3\alpha)$$

where E_{THz}^x and E_{THz}^y are the projection of THz electric field along the x and y axis. The sinusoidal dependence is confirmed by the two-dimensional (2D) mapping of THz electric field peak as a function of θ and α , as shown in Figure S1. Note that only the vertical component (x projections) of the emitted THz pulses are detected in the present study. The excellent consistency between the experimental data and theoretical anticipations supports the shift-current origin of THz emission from Bi_2Se_3 films.

Section S2: Power dependence of THz emission.

Figure S2. Co thickness dependence of SCC components. Extracted SCC components of the measured THz waveforms from Bi_2Se_3 (10 QL)/Co heterostructures with different Co thicknesses. The waveforms are shifted horizontally for clarity.

We have performed the power dependence measurements for Bi_2Se_3 (10 QL) film. As a second-order nonlinear effect, the THz peak amplitude is expected to be proportional to the

incident pump power. However, it exhibits a saturation behavior as indicated in Figure 1d in the main text. The observed nonlinearity probably stems from saturable absorptions,^[10] which is commonly described by the intensity dependent absorption coefficient: $\alpha(I) = \alpha_0/(1 + I/I_{sat})$, where α_0 is the unsaturated absorption coefficient, I is the input laser intensity, and I_{sat} is the saturation intensity. The THz radiation originates from the instantaneous transfer of photoexcited charge carriers, and thus it should be proportional to the absorbed pump power: $E_{THz}^x \propto \alpha(I) \cdot I$. Therefore, we can expect: $E_{THz}^x \propto P/(P + P_{sat})$, where P is the incident pump power and P_{sat} is the saturation power. As shown in Figure 1d in the main text, the saturable absorption model can quantitatively explain the data. The mechanism of saturable absorption can be explained by Pauli blocking principle, as has been widely investigated in graphene.^[11]

In contrast to the pure Bi₂Se₃ films, the peak amplitude of THz signal from Bi₂Se₃ (10 QL)/Co (3 nm) heterostructure increases linearly with the excitation power at low incident power region (<40 mW), as shown in the inset of Figure 2d in the main text. This is consistent with the expectation for spin-current injection from the ferromagnetic layer. The injected spin current is proportional to the number of photoexcited carriers, and hence proportional to the incident pump power. This provides further evidence that spin-to-charge conversion is the main mechanism of THz emission in the heterostructures. For higher incident power above 40 mW, there is a slight deviation from the linearity. In the present study, THz emission from both Bi₂Se₃ films and Bi₂Se₃/Co heterostructures were measured by using 60 mW pump power unless noted otherwise.

Section S3: Qualitative picture of the dynamics of intermediate energy carrier multiplication.

We here describe qualitatively what is the physical picture behind the delay of 0.12 ps between the shift current-driven peak and the spin diffusion-driven one. In Figure S3 we show

how the excited carriers in the whole bilayer evolve in time (we do not show the spatial profile).^[12] Before the laser excitation, there are no excited carriers above the Fermi energy (thermally activated carriers can be safely neglected). a) When the laser pulse arrives, electrons are excited to energies that go from the Fermi energy all the way up to the photon energy. These excited carriers start producing a spin current. b) At the peak of the laser excitation more electrons are excited and a larger spin diffusion takes place. c) However, the excited electrons do not survive at high excitation energies for long times. When they scatter they lose energy and excite another electron from below the Fermi energy, which will in turn participate to the diffusion. This effect is known as excited carrier multiplication upon scattering, since each scattering will transform a high energy electron into two intermediate energy ones. Interestingly each intermediate energy electron induces a much more efficient spin diffusion than high energy ones: while the spin polarization of the diffusion is proportional to the spin asymmetry in the transport properties, the overall amplitude is proportional to the mean free path of the carriers. High energy electrons, irrespectively of the spin asymmetry, tend to have particularly short lifetimes (see right panel in Figure S3), making their mean free path, and consequently, their diffusion very small. Instead intermediate energy electrons have importantly longer lifetimes, and a very effective diffusion, which is also happens to be strongly spin polarized. d) The peak of the spin current happens when high energy excitations have created a large number of intermediate energy excitations. e) Eventually the excited electrons lose their energy to phonons and the spin diffusion will decrease in amplitude.

The peak of the spin diffusion is therefore delayed compared to the shift current (which follows the laser time profile) one. This time delay depends, through the lifetimes, only on the material in which the carriers thermalize, and not on the layer thickness (unless there is a

distance of at least several hundreds of nanometers between the laser excitation region and the heavy element material).

Figure S3. Qualitative picture of the dynamics of intermediate energy carrier multiplication. The top left panel shows the energy distribution of the excited energy evolving in time. The number of dots represents the carrier concentration. The middle panel shows the time profile of the laser pulse. At the bottom is the time profile of the amplitude of spin diffusion through the FM/TI interface. The right panel shows the spin dependent lifetimes on which the effectiveness of the spin diffusion strongly depends.

Section S4: Exclusion of ISHE contribution.

If the inverse spin Hall effect was to play a major role in the spin-to-charge conversion processes in our heterostructure, the resulting 2D charge current after integration over the thickness of the ISHE layer can be described as:^[13,14]

$$J_c = \langle j_c \cdot d \rangle = \theta_{SH} \lambda_{sf} \tanh\left(\frac{d}{2\lambda_{sf}}\right) j_s \quad (S1)$$

where j_s and j_c are the injected spin current and resulting charge current, θ_{SH} is the spin Hall angle, d is the thickness of Bi_2Se_3 films, and λ_{sf} is the spin diffusion length in Bi_2Se_3 . Thus, the electric field of the emitted THz radiation should be:

$$E_{THz}(t) \propto \frac{\partial J_c}{\partial t} \propto \theta_{SH} \lambda_{sf} \tanh\left(\frac{d}{2\lambda_{sf}}\right) \frac{\partial j_s}{\partial t} \quad (S2)$$

In the limit of $d < \lambda_{sf}$, Equations S1 and S2 can be written as:

$$J_c = \frac{1}{2} \theta_{SH} \cdot d \cdot j_s \quad (S3)$$

$$E_{THz}(t) \propto \theta_{SH} \cdot d \quad (S4)$$

This means that, in very thin films (and even if $d \sim \lambda_{sf}$ — see Figure S4 and its caption), the measured THz signal should be proportional to the thickness of Bi_2Se_3 film. However, our experimental data do not show this dependence, as shown in Figure S4, where the peak amplitude of THz signal contributed by SCC component increases about one order of magnitude when the Bi_2Se_3 thickness increases from 4 to 6 QL, and then remains roughly constant for 6 to 10 QL. To further clarify this issue, we follow the analysis of Ref. [15] to fit the THz peak amplitude (4 to 10 QL) with a tanh function:

$$E_{THz}(t) = A \tanh\left(\frac{d-2}{2\lambda_{sf}}\right) \quad (S5)$$

where A is a fitting parameter and d is the thickness of Bi_2Se_3 film. However, equation S5 still cannot fit our experimental data, as shown in Figure S4.

Since IEE can be described by^[14,16]

$$J_c = \lambda_{IEE} \cdot j_s \quad (S6)$$

where the IEE length λ_{IEE} is a measure of the SCC efficiency, by comparing Equations S3 and S6, we can get an approximate relationship between the spin Hall angle θ_{SH} and the IEE length λ_{IEE} as:

$$\lambda_{IEE} = \frac{1}{2} \theta_{SH} \cdot d \quad (S7)$$

Figure S4. Fit with tanh function. The extracted SCC THz peak (blue squares) and that normalized by the THz pump transmittance (orange circles), as a function of Bi₂Se₃ thickness. The solid lines (blue and orange) show the fits with $y = A \cdot \tanh\left(\frac{d-2}{2\lambda_{sf}}\right)$, where A is a fitting parameter, d is the thickness of Bi₂Se₃, and λ_{sf} is the spin diffusion length. This function cannot fit our data, let alone $y = A \cdot \tanh\left(\frac{d}{2\lambda_{sf}}\right)$. The green solid line is a plot of the function of $y = 5 \cdot \tanh\left(\frac{d}{2\lambda_{sf}}\right)$, where $\lambda_{sf} = 2$ QL. It shows that even when the condition $d < \lambda_{sf}$ is not strictly satisfied, i.e. at $d = \lambda_{sf}$ (green dashed line), the relationship between the emitted THz amplitude and Bi₂Se₃ thickness is still approximately linear, justifying the use of Equations S3 and S4 in our heterostructures.

Section S5: THz absorption in Bi₂Se₃ films.

The extracted THz waveforms contributed by SCC component, as illustrated in Figure S5a, decrease gradually with thicker Bi₂Se₃ films (above 10 QL). Since the SCC processes via IEE occur at the top surface of Bi₂Se₃ film, the resulting THz pulses go through the bulk of Bi₂Se₃ film where it can be absorbed by the free carriers in the bulk. Figure S5b shows the THz electric field transmittance spectra of Bi₂Se₃ with different thicknesses from 4 to 40 QL. The equilibrium transmittance decreases with increasing the film thickness indicating the existence of intrinsic carriers in the bulk. Additionally, as has been discussed in the main text, the THz emission contributed by the injected spin current via IEE lags the pump beam about 0.12 ps which is shorter than the lifetime of the photo-generated carriers,^[17] and hence can be also absorbed by these pump-induced carriers in Bi₂Se₃ films. To verify this hypothesis, we have performed the optical-pump THz-probe experiments on pure Bi₂Se₃ films at a fixed pump power of 30 mW, considering that the transmittance of the 4 nm-thick Co layer at 800 nm is ~50%. The relative changes of the THz transmittance as a function of pump delay time are shown in Figure S5c for Bi₂Se₃ films with different thicknesses. The data are collected with the gating beam at the peak of the equilibrium THz waveform. Indeed, the amplitude of THz transmittance decreases for thicker films because it excites more carriers in the bulk.^[18] Based on the equilibrium THz transmittance at 1 THz (corresponding to the peak of THz

waveform) and the maximum change of transmittance upon excitation, we obtain the THz electric field transmittance of Bi_2Se_3 upon optical excitation, as shown in Figure 4a in the main text and Figure S5d, which is the transmittance of the THz pulses that were generated by IEE at the interface of TI/FM heterostructure when propagated through the bulk of Bi_2Se_3 film.

Note that, we did not take the carriers absorption into consideration for THz emission from pure Bi_2Se_3 films considering the following facts. Firstly, for the pure Bi_2Se_3 films, the THz transients originate from the shift of the center of charge within the unit cell during the optical excitation, and hence cannot be absorbed by the photo-generated carriers themselves. Secondly, as a second order nonlinear effect, the THz emission occurs on both sides of the film. Only the THz transients generated from the top surface propagate through the bulk, while that from the bottom surface directly goes through the substrate and hence do not experience the absorption in the bulk.

Figure S5. Bi_2Se_3 thickness dependence. (a) The extracted SCC waveforms for $\text{Bi}_2\text{Se}_3/\text{Co}$ (4 nm) heterostructures with different Bi_2Se_3 thicknesses. (b) Equilibrium THz electric field transmittance spectra of Bi_2Se_3 films with different thicknesses. The dip around 2 THz corresponds to the optical phonon mode in Bi_2Se_3 . (c) The minus differential transmittance

optical-pump THz-probe data of Bi_2Se_3 films with different thicknesses at a fixed pump power of 30 mW. The lines are slightly shifted horizontally for clarity. The hump at ~ 7 ps is due to the back-reflection of the pump beam. (d) The peak amplitude of the extracted SCC components from $\text{Bi}_2\text{Se}_3/\text{Co}$ (4 nm) heterostructures (red dots) and THz transmittance amplitude of Bi_2Se_3 films under a pump power of 30 mW (blue dots), as a function of Bi_2Se_3 thickness. This is the same figure as Figure 4a in the main text.

Section S6: Temperature dependence of THz emission.

Here we show the temperature dependence of THz radiations from both Bi_2Se_3 (10 QL) film and Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure. For Bi_2Se_3 thin film, the measured THz peak amplitude increases about 2.3 times as the temperature decreases from 300 to 10 K, whereas the waveforms remain unchanged, as shown in Figure S6a. The temperature dependence of THz emission shows a similar behavior to that of the carrier mobility that obtained from the Hall measurement, indicating that the enhancement of THz emission is due to the increase of carrier mobility at low temperature. This can be explained by the fact that the photoexcited carriers would experience multiple electron-phonon scattering events before they relax back to the equilibrium distribution.^[19] Therefore, the scattering processes exert considerable influence on the relaxation of these photoexcited carriers and hence the resulting THz radiations.

Figure S6. Temperature dependence of THz emission. (a) The peak amplitude of THz signals and Hall mobility versus temperatures for Bi_2Se_3 (10 QL) film. The inset shows the detected THz waveforms at representative temperatures. (b) Temperature dependence of THz peak amplitude for Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure. The filled triangles represent the THz peak amplitude measured at polarization angle $\theta = 0^\circ$ and 90° . The filled circles and

squares represent the extracted THz peak amplitude of the SCC and TI (shift-current) components, respectively.

The temperature dependence of THz signal from Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure are plotted in Figure S6b. The THz peak amplitudes of the extracted SCC component, are almost temperature independent, while the extracted TI components, namely, the shift-current components, have a similar temperature dependence to that from pure Bi_2Se_3 film. This result also supports the idea of that the measured THz signal from the heterostructure is a superposition of the two separate contributions.

Figure S7. A comparison between THz signals from Pt/Co and TI/Co heterostructures. Measured THz waveforms for Pt (2 nm)/Co (3 nm), Pt (6 nm)/Co (3 nm) and Bi_2Se_3 (10 QL)/Co (3 nm) heterostructures under identical experimental conditions.

Section S7: Estimation of spin current density.

In this section, we estimate the amplitude of injected spin current from Co into Bi_2Se_3 . Following Ref. [20], the THz electric field strength from the Bi_2Se_3 (10 QL)/Co (3 nm) heterostructure can be obtained to be ~ 0.15 kV/cm. As discussed in the main text, SCC occurs at the interface of TI/FM bilayer structure, thus the resulting THz pulses have to traverse through the TI bulk and the substrate in order to be detected (see Figure 2a). The THz transmittance of 10-QL Bi_2Se_3 film under optical pump is 95.5%, as shown in Figure S5. The

measured THz transmittance of 0.5-mm thick sapphire is 72%. Consequently, the peak electric field strength of THz radiation generated at the Bi₂Se₃ (10 QL)/Co (3 nm) interface is $0.15/(0.955 \times 0.72) = 0.22$ kV/cm. From this, we then obtain the charge current density using the generalized Ohm's law $E(\omega) = -\frac{Z_0}{1+n}J(\omega)$,^[21] where $Z_0 = 377 \Omega$ is the vacuum impedance and $n(\omega)$ is the refractive index on the surface of Bi₂Se₃ film. We follow Ref [22] and derive $n(\omega = 1 \text{ THz}) \approx 50$, then the peak surface THz current is

$$|J_{c,peak}| = \frac{1+50}{377 \Omega} \times 0.22 \frac{\text{kV}}{\text{cm}} = 29.8 \text{ A/cm}.$$

Finally, we obtain the peak spin current density from Equation S6,

$$j_{s,peak} = \frac{J_{c,peak}}{\lambda_{IEE}} = \frac{29.8 \text{ A/cm}}{50 \text{ pm}} = 6.0 \times 10^9 \text{ A/cm}^2$$

Using the same procedure, the electric field strength of THz radiation from Pt (2 nm)/Co (3 nm) heterostructure is estimated to be 0.13 kV/cm. Since the refractive index of Pt film is ~ 80 ,^[23] the peak surface charge current is then $J_{c,peak}^{Pt} \sim 27.9$ A/cm and hence the three-dimensional peak charge current density $j_{c,peak}^{Pt} = \frac{J_{c,peak}^{Pt}}{t_{Pt}} = 1.4 \times 10^8$ A/cm². Finally, the peak spin current density $j_{s,peak}^{Pt} = \frac{j_{c,peak}^{Pt}}{\theta_{SH}^{Pt}} = 4.7 \times 10^9$ A/cm². Thus the spin current density injected into 10-QL-thick Bi₂Se₃ (6.0×10^9 A/cm²) is roughly the same as that into the 2-nm-thick Pt film (4.7×10^9 A/cm²), and also has the same order of magnitude as that obtained from the Fe (10 nm)/Au (2 nm) heterostructure (1.3×10^9 A/cm²).^[24] This supports our assertion in the main text that the injected spin current density for Pt (2 nm)/Co (3 nm) and Bi₂Se₃ (10 QL)/Co (3 nm) heterostructures are similar under identical experimental conditions.

References for Supporting Information

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