# ENERGY TRANSPORT IN THIN-FILM TOPOLOGICAL MATERIALS

by

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Dedicated to my mom and dad

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### ABSTRACT

Solid-state thin films are vastly involved in the advanced electronics industry and emerging condensed-matter physics research. The perspective of energy carriers plays a key role of understanding heat transfer physics in nanoscale thin films, also introduces numerous experimental and numerical tools. Topological materials are a new phase of condensed matter, with topologically nontrivial electron states emerged on whose boundary. The topological state electrons possess unique carrier dynamics and spin polarization, leading to unconventional energy transport performance and the possibility for controlled heat transfer, which is largely unexplored. Thin films three-dimensional topological insulators are a good platform to investigate topological surface states due to the large surface to bulk ratio.

In this doctoral work, optical, electrical, and thermal methods are incorporated to study the energy transport carried by topological surface state electrons. The optothermal micro-Raman thermometry method was applied to measure the thermal conductivity of topological insulator thin films. The surface states in sub-20-nm were found dominant in charge and energy transport, and an extraordinary large Lorenz number was identified. The thermal conductivity of Weyl semiconductor 2D-tellurium, another topological material, was similarly studied. A comprehensive calibration method was proposed to resolve the complication of temperature/strain Raman responses in the presence of thermal expansion during micro-Raman thermal conductivity measurement. Photocurrent under circular polarization incidence was studied to understand topological surface states transport characteristics under optical spin injection. The level of helicity-tunability of topological surface states was optimized and deep tuning of photothermoelectricity from surface states was observed. The helicity-dependent photoconductance was also discovered to be a competitive candidate for optical chirality detection, and single-device Stokes parameters analyses were implemented using a Bi<sub>2</sub>Te<sub>2</sub>Se phototransistor. Lastly, micro-Raman thermometry and fabrication techniques for vacuum or optical gating are combined to perform gate-dependent thermal conductivity measurement for nanometer thin films. Gatedependent thermal conductivity of thin-film topological insulators is studied and the large contribution from topological surface state is found electrostatically tunable. The results lead to an implementation of solid-state electrostatic thermal transistors with large ON/OFF ratio and fast

switching time. Temperature dependence of the gated-tunable heat transport is also studied for further understanding of the topological states in heat transport.

Thermal energy transport phenomena in topological materials are approaches from both directions of metrology and dynamic control. The studies demonstrate the intriguing behaviors of topological states and also indicate the implementation of optical and thermal devices with exotic functionalities.

### **1. INTRODUCTION**

Solid-state thin films are vastly involved in the advanced electronics industry and emerging condensed-matter physics research. The structures in most electronic, optoelectronic, and microelectromechanical systems are patterned by planar processes so that thin films are widely used building-blocks. Curiosities on heat at the small scale naturally rises. As the device structure scaling down to the nanoscale, the power density increases, also the thermal properties are affected by the geometries and dimensions. It makes a critical task to study the heat transfer performance at the nanoscale, and the energy carrier perspective, i.e., electrons and phonons in solids, is essential to understand the size effects. Beyond the more effective heat dissipation in electronic devices with nanostructures, which aimed at enhancing the heat conduction, the knowledge on nanoscale energy carriers can also help to suppress the heat conduction. For example, in thermoelectric generators for waste heat recovery, the thermoelectric material is engineered that, the thermal conductivity is reduced by suppressing the phonon transport to maintain the temperature difference, while the electrons transport is untainted and thus the electrical performance preserved.

Topological materials are a new phase of condensed matter, named after the mathematical formalism of their electron wavefunction is topologically distinctive from that in normal solids. The topologically non-trivial electron states exhibit intriguing behaviors, e.g., in topological insulators, the bulk (trivial) electrons are gapped insulators/semiconductors and the topological surface states are gapless spin-non-degenerated Dirac states with backscattering prohibited. The thermal properties of the topological states are scientifically significant and the possibility in spin-control opens a way to nanodevices for thermal controlling.

In this chapter, we first revisit the physics of electrons and phonons and their contribution to heat transfer. Next, we equip ourselves with the experimental techniques of thin-film thermal conductivity measurement and topological state controlling. Following is an introduction to topological insulators and the topological surface states, including the methods to control the states. The content of this chapter is mainly based on Refs (Fisher, 2013; Hasan & Kane, 2010; Kittel & McEuen, 1996; Shen, 2017)

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#### 1.1 Thermal Energy at the Nanoscale: Electrons and Phonons in Solids

#### 1.1.1 Phonons and electrons as energy carriers

Phonons and electrons are the common energy carriers in most solids. Phonons are quantized modes of vibration in solids. The phonons with longer wavelengths are essentially the sound wave. Per the wave-particle duality of the quantized quasi-particle, each phonon has energy  $E_{\rm ph} = \hbar \omega$  associated with the frequency  $\omega$  and a momentum  $p_{\rm ph} = \hbar K$  associated with the wavevector  $K = \frac{2\pi}{\lambda}$  or the wavelength  $\lambda$  ( $\hbar$  is the Planck constant). The relation between the energy and momentum (for phonons frequency vs. wavevector is more often used) is called the dispersion relation and the slope is the group velocity. In crystalline solids, phonons can be rigorously treated in the reciprocal space, i.e., the spatial Fourier space of the real lattice, and the dispersion relation can be demonstrated in the Brillouin zone of the reciprocal space. The modes with similar vibration patterns form a continuous branch in their dispersion relations. Figure 1.1 shows an example of the dispersion relation of silicon, in which the solid lines are theoretical calculation results (Zhou et al, 2014) and the dots are experimental results using neutron scattering spectrometry (Dolling, 1963). There are two types of phonons, acoustic phonons (denoted by A) and optical phonons (O). Acoustic phonons have near-linear dispersion, and asymptotically to the speed of sound wave at low frequency. Optical phonons exist only when more than one atom in a unit cell, creating a time-varying electrical dipole moment and thus active to optical excitation. The frequencies are higher (usually in mid-infrared range), and the dispersion is usually flat. The optical mode with near-zero momentum can be probed directly by infrared spectroscopy or indirectly by Raman spectroscopy. The group velocity  $v_g = \frac{d\omega}{dK}$  is the actual speed that a wave packet propagates. The group velocities of acoustic phonons are usually larger.



Figure 1.1 Phonon dispersion of silicon. Reprinted with permission from (Zhou et al., 2014). Copyright (2014) American Physical Society.

Conducting electrons in solids depend on the filling states of the atomic orbitals. The traveling electron wave within the periodic potential of the atom lattice (Bloch wave) scatters with the lattice and opens gaps between the energy bands where no states is allowed. The energy level that the electrons fill till at 0K is called Fermi level E<sub>F</sub>, and more generally at a finite temperature the chemical potential  $\mu = E_{\rm F} \left[ 1 - \frac{1}{3} \left( \frac{\pi k_{\rm B} T}{2E_{\rm F}} \right)^2 \right]$ , k<sub>B</sub> is the Boltzmann constant. The thermal energy that an electron carries is the difference to the chemical potential  $E-\mu$ . For metals, the energy bands are half-filled or overlapped that the electrons can freely move and exchange momentum near the chemical potential  $\mu$ . When electrons filled till the bandgap, the exchange of momentum and energy is prohibited due to Pauli exclusion, i.e., the electrons cannot move, and the solids thus called (general) insulators. At finite temperature, electrons can be ionized, making conducting holes (void of electrons as a positive-charged particle with positive effective mass) at the edge of the lower energy band (valence band) and conducting electrons higher energy band (conduction band), thus electron motion is allowed. Depending on the bandgap and the chemical potential alignment to the band, the density of mobile electrons may vary by a few orders of magnitude and the solids are called (special) insulators or semiconductors per the resulting conductivity. In crystalline materials, the dispersion relation (or band structure) can also be presented in the Brillouin zone. The concept of group velocity holds true for electrons, and the value at the Fermi

level is called Fermi velocity  $v_F$ . Electrons in most solids are still massive but the effective mass differs from the value in the free space for reasons such as: interaction with periodic potential field i.e., the energy band effective mass; electron-phonon interaction when conducting electron deforms the polarization of the lattice and drags the adjacent ions; correlations between electrons, i.e., the manifest inertia reacting force from the electron sea.



Figure 1.2 Electronic band structure of silicon. Reprinted with permission from (Sano & Yoshii, 1992), Copyright (1992) American Physical Society.

#### 1.1.2 Carrier statistics and thermal energy storage

The energy stored in the carriers depends on the carrier density and state statistics. Phonons are Bosons, i.e., indistinguishable particles with the spin of integer and following Bose-Einstein distribution  $f^0 = \frac{1}{\exp \frac{\hbar \omega}{k_B T} - 1}$  at thermal equilibrium at temperature *T*. In most systems, the coherence of phonons does not pronounce i.e., wave effect of phonon is negligible, the phonons can be treated as colliding particles following Boltzmann distribution  $f^0 = \exp - \frac{\hbar \omega}{k_B T}$ . The general form of phonon thermal capacity is given as Eq. 1.1 by summing up all the kinetic energy of all the phonon modes.

In crystalline solids, the allowed states, i.e., the supported harmonic oscillators in the lattice, are evenly distributed in the reciprocal space (with a spacing of  $2\pi/L$ , L is the dimension of the solid) and thus the number of states can be analyzed by the occupied "volume". The concept of density of states (DOS) with respect to the energy/frequency is introduced, i.e., the "surface area" of the region of the allowed states. The density of excited phonon states that store the energy is thus the product of DOS and  $f^0$ . Now the summation in Eq. 1.1 can be evaluated by an integral of energy/frequency. For instance, the density of states (per unit volume) of phonons in an isotropic 3D lattice, and the heat capacity are given in Eq. 1.2 and 1.3. The summation over p is for longitudinal (L), traverse (T), and/or flexural (Z, i.e., out-of-plane) polarizations.

$$c_{\rm v,ph} = \frac{1}{V} \sum \frac{\partial f^0}{\partial T} \hbar \omega \tag{1.1}$$

$$DOS_{\text{ph,3D}}(\omega) = \frac{\frac{\mathrm{d}N}{L^3}}{\mathrm{d}K} \frac{\mathrm{d}K}{\mathrm{d}\omega} = \frac{\mathrm{d}\frac{4\pi K^3/3}{(2\pi/L)^3 L^3}}{\mathrm{d}K} \frac{1}{\mathrm{d}\omega/\mathrm{d}K} = \frac{K^2}{2\pi^2} \frac{1}{v_{\mathrm{g}}}$$
(1.2)

$$c_{v,ph} = \sum_{p} \int \hbar \omega DOS(\omega) \frac{\partial f^{0}}{\partial T} d\omega$$
(1.3)

Electrons are distinguishable particles with the spin of 1/2, categorized as Fermions and follow the Fermi-Dirac distribution  $f_{FD}^0 = \frac{1}{\exp \frac{E-\mu}{k_B T}+1}$  at thermal equilibrium at temperature *T*. The general form of carrier density and electronic thermal capacity can be similarly obtained but summing up the thermally excited states. The density for electrons and holes is obtained by integrating the conduction/valence band (CB/VB) as Eq. 1.4), and the electronic heat capacity is given similarly as in Eq. 1.4. Notice the Pauli exclusion principle is satisfied in the Fermi-Dirac distribution, and the Boltzmann distribution is an oversimplification that fails to predict the electronic thermal capacity.

n, p = 
$$\int_{CB,VB} (E - \mu) \frac{\partial f_{FD}^0}{\partial T} DOS(E) dE$$
(1.4)

$$c_{v,e} = \int (E - \mu) \frac{\partial f_{FD}^0}{\partial T} DOS(E) dE$$
(1.5)

The introduction in this section is mostly based on Ref. (Fisher, 2013; Kittel & McEuen, 1996)

#### 1.1.3 Scattering of carriers and thermal energy transport

Scattering of the carriers (or collisions in the particles' perspective) is the dissipation factor of the carrier transport in the channel. When the carriers do not experience scattering, the conduction is independent of the length of the channel and called the ballistic transport process. The scattering process randomizes the motion, reducing the momentum along the driving gradient and thus suppress the carrier transport. The Fermi's Golden rule, derived from quantum mechanical time-dependent perturbation theory, is a generic way for any scattering processes to evaluate the probability transition rate  $\dot{\gamma}(\mathbf{p}_i, \mathbf{p}_f)$  from a specific initial  $\mathbf{p}_i$  to final state  $\mathbf{p}_f$ . The mostadopted treatment for scatterings is using the relaxation time  $\tau$  (Eq. 1.6a, considering the scatter rate and occupancy of the final state  $f(\mathbf{p}_f)$ ) and the overall relaxation rate is obtained by Matthiessen's rule (Eq. 1.6b), i.e., the scattering mechanisms are treated as admittances in series. Several scattering mechanisms are well-formulated, and the models are introduced as follows.

$$\tau(\boldsymbol{p}_{\rm i})^{-1} = \sum_{\boldsymbol{p}_{\rm f}} \dot{\gamma}(\boldsymbol{p}_{\rm i}, \boldsymbol{p}_{\rm f}) \left(1 - f(\boldsymbol{p}_{\rm f})\right)$$
(1.6a)

$$\tau_0^{-1} = \sum \tau^{-1}$$
 (1.6b)

Both electrons and phonons scatter with boundary or material interfaces and the contribution depends on its specularity p. p = 1 represents a specular boundary, i.e., the collisions are elastic and do not resist the conduction while p = 0 is a diffuse boundary that randomizes the reflected carrier and created resistance to the conduction. E.g., the boundary scattering rate in a thin film with a characteristic length of L can be modeled as  $\tau_{\text{boundary}}^{-1} = (1 - p)v/L$ .

Impurities and defects are another source of scattering. The Rayleigh law  $\tau_i^{-1} = A\omega^4$  gives a good estimation for phonon scattering with point defects. While electrons are more complicated because of varied cases of Coulomb interaction and local states. Besides the boundaries and impurities/defects, there are intrinsic scattering mechanisms happening even in perfect crystals.

Phonon-phonon scattering arises from anharmonicity of the interatomic potentials. One phonon may split into two or more, or reversely multiple phonons merge into one, satisfying momentum and energy conservation. The reciprocal lattice vector may also kick in to the momentum conservation and create resistance. Take three-phonon scattering for example, as shown in Figure 1.3, the conservation of momentum requires  $K_1 + K_2 - K_3 = G$ . (Kittel & McEuen, 1996) The lattice cannot support a phonon wavelength short than two lattice constants and thus the post-scattering momentum is brought back to the Brillouin zone with a non-zero G, reducing the heat conduction. This process is called the Umklapp process. The normal processes with G = 0, though do not directly resist the conduction, recover the phonons wavevectors for possible Umklapp processes, hence cannot be neglected. The phonon-phonon scattering rate increase with temperature since more phonons are excited. Above the Debye temperature, i.e., the temperature where all the acoustic modes are excited,  $\tau_{\rm U}^{-1} = B\omega^2 T$  is one of the common-used models.



Figure 1.3 Three-phonon scattering process. (a) normal process. (b) Umklapp process

The consequences of electron-phonon scattering and electron-electron scattering, though negligible in thermal transport in many materials, are more complicated and a unified model is yet available. The quantitative result is only available with theoretical calculations. It's worth noticing that, Fermi's Golden rule points out certain scattering process is not possible when the initial and the final states are orthogonal under the perturbation Hamiltonian with given symmetries. It provides a qualitative understanding of e.g., the anisotropy of materials properties (Sadasivam, Chan, & Darancet, 2017), and the non-reciprocity of topological materials (Hasan & Kane, 2010).

Specific to electronic systems, the relaxation of electrons not only involves with the randomization in the momentum space, also the recombination of the electron-hole pairs. The significance of the difference between momentum and energy is mostly addressed in systems with generation (optoelectronics) or operating far from equilibrium e.g., impact ionization MOSFETs or other high-field electronics (Bulutay, Ridley, & Zakhleniuk, 2003; Lundstrom, 2000). On the

other hand, this difference is also critical when involving energy transfer, e.g., thermoelectric effect and electronic thermal conductivity. The momentum relaxation of electrons mostly relies on the mechanism introduced above. While the energy relaxation involves varied procedure (Pierret, 2003) including the phonon and dopant-levels assisted recombination, also direct process (or called radiating recombination since an photon is emitted at the energy of the bandgap, and the emission after external photo-excitation is called photoluminescence, PL) and Auger effect (the recombination process filling the inner-shell vacancy accompanied by a spontaneous excitation of another electron(s) to higher energy state(s)). Also notice a collision that flips the momentum of an electron may not change its kinetic energy, i.e., the final state  $p_{\rm f}$  may on the same energy level to  $p_i$ . The result of these scatterings interrupts the momentum transport while energy-wise the carriers remain out of equilibrium. Thus, the effective relaxation rates of electrons in terms of the momentum and energy differ, and more than one relaxation times (or mean-free-path) are needed to depict the charge and thermal energy transport process. For example, when generated electronhole pairs travel all the way through the channel and recombine to release the energy at the other end, no net charge yet thermal energy is transferred (called bipolar diffusion transport (Goldsmid, 1956; Goldsmid, 2010; Yoshino & Murata, 2015)). Reducing the (energy) relaxation rate of this process enhances the electronic energy transport, but electrical charge conduction is left untouched. Another example is to design energy filters (Dresselhaus, et al., 2007; Hicks & Dresselhaus, 1993) for thermoelectric based on the energy relaxation length.(Moyzhes & Nemchinsky, 1998; Thesberg, Kosina, & Neophytou, 2016)

The kinetic theory provides a simpler treatment of the transport properties. Given the relaxation time (or the mean-free-path  $\Lambda = v\tau$ , i.e., the temporal and mode-wise average of the free traveling distance between collisions), and averaged velocity v, the thermal conductivity can be derived by considering the net energy flux through a control surface. In the 3D case (effective velocity on the direction of the temperature gradient is averaged over a hemisphere), the thermal conductivity of phonons/electrons share a unified form Eq. 1.7. When the dimension of the conduction channel L is not much larger than the mean-free-path, the additional scattering at the boundary will reduce the  $\Lambda$  and thus suppress the thermal conduction. This is called classical size effect, distinguished from the quantum size effect where the coherence of the propagating wave is affected by the channel size. A transmission factor  $T = \kappa(L)/\kappa_{\text{bulk}} = \Lambda/(L + \Lambda)$  gives a simple estimation of the classical size effect and abridges the diffusion (bulk) and ballistic limit. This

simple picture comprises the determining factors of thermal conductivity: the thermal capacity related to the density of states, the mean-free-path or the relaxation time related to the scattering, and the group velocity, related to, e.g., bond stiffness for phonons, effective mass for electrons, etc.

$$\kappa_{\text{bulk}} = \frac{1}{3}c\Lambda v_{\text{g}} = \frac{1}{3}cv_{\text{g}}^{2}\tau \tag{1.7}$$

The kinetic theory also leads to a direct connection between electronic thermal and electrical conductivity ( $\sigma$ ). When the effective mass ( $m_e$ ) and the relaxation time are both identical in charge and thermal energy transfer process, the ratio of thermal and electrical conductivity divided by the temperature, defined as the Lorenz number  $L \stackrel{\text{def}}{=} \frac{\kappa_e}{\sigma T}$ , is a constant. This relation is called the Wiedemann-Franz law. E.g., in metals, with  $\sigma = \frac{\rho_e e^2}{m_e} \tau$  ( $\rho_e$  is the charge carrier density),  $c_{v,e} = \pi^2 \rho_e k_B T / 2E_F$ , and  $E_F = \frac{1}{2} m_e v_F^2$ , the Lorenz number is calculated to be  $L_{metal} =$  $\frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8} W \Omega K^{-2}$ , and this value is called the Sommerfeld value. The Lorenz number of a single-band non-degenerate semiconductor can be similarly calculated to be  $L_{semi}$  =  $1.5 \times 10^{-8} W\Omega K^{-2}$ . The Lorenz number of most solids range between these two values depending on its band structure and degeneracy. However, exceptions can be made when the effective mass or relaxation in charge and heat transport are distinctive, e.g., the Lorenz number in heavy Fermion UBe<sub>13</sub> is temperature-dependent and much exceed the Sommerfeld value. Another example of violation of Wiedemann-Franz law is due to the large difference of the relaxation process in hydrodynamic electronic systems. A viscosity (i.e. near-diffusive momentum relaxation) of charge transport emerged from the strong electron-electron interaction while the thermal transport is limited only by the energy relaxation out of the conventional scattering mechanisms. (Foster & Aleiner, 2009; Lee et al., 2017; Müller, Fritz, & Sachdev, 2008; Principi & Vignale, 2015) A 20fold increase of the Lorenz number is observed in graphene ~75 K.(Crossno et al., 2016) A violation of the Wiedemann-Franz law is also observed in the topological surface states originate from the unconventional scattering mechanism and will be discussed in Section 2.2.

In real solids, the contribution of carriers may vary vastly depending on their specific states, beyond the capability of the kinetic theory model, and the detailed knowledge in their mode-wise behavior is essential to make high-fidelity predictions and to engineer novel materials. To unravel the mode-wise information, the carriers can be treated in two equivalent ways, Boltzmann transport, and Landauer formalism.

The Boltzmann transport equation (BTE, Eq. 1.8) is a natural result of the Liouville equation for statistical systems out of equilibrium.

$$\frac{\partial f}{\partial t} + \boldsymbol{\nu} \cdot \nabla_{r} f + \frac{\boldsymbol{F}}{m} \cdot \nabla_{\nu} f = \left(\frac{\partial f}{\partial t}\right)_{c} = -\frac{f - f^{0}}{\tau}$$
(1.8)

The F is the force acting on the particle. The right-hand side term of the first equal mark is in fact a collision integral with the dimension of distribution over time. The practical way to evaluate carrier transport is to evaluate the relaxation time to recover to equilibrium, then to solve the BTE with the right-most term. Besides extracting the apparent thermal conductivity for thin films and nanowires, BTE can be discretized and numerically solved in the control volumes for more complex geometries, similar to the other continuum partial differential governing equations.

On the other hand, the Landauer formalism sees any type of conduction as transmission, i.e., the consequence of the carriers injected to the channel under the driven force and the probability to reach the other end. In heat transfer, i.e. temperature-driven thermal energy transport, the conductance provided by each transmitting mode (called the quantum of thermal conductance) of acoustic phonons and electrons (single parabolic band) are  $\hat{\Gamma}_{ph} = \frac{\pi k_B^2 T}{6\hbar}$  and  $\hat{\Gamma}_e = \frac{\pi k_B^2 T}{3\hbar}$  (the factor of 2 is due to spin degeneracy), respectively. The density of transmitting modes (DOM) is the product of the cross-section, the DOS, and averaged velocity projected in the direction of transport, e.g.,  $DOM_{3D} = A \times \frac{\pi}{2} v_g \times D_{3D}$  by averaging the velocity over the hemisphere. The transmission coefficient  $\mathcal{T}$ , indicating the probability of a carrier in each channel to reach the other contact, is obtained considering all the scattering mechanism for each mode, and  $\mathcal{T}=1$  when ballistic. The electron and phonon thermal conductance in Landauer formalism are as Eq. 1.9.

$$\Gamma_{ph} = \frac{1}{2\pi} \int DOM(\omega) \hbar \omega T \frac{\partial f_{BE}^0}{\partial T} d\omega$$
(1.9a)

$$\Gamma_{el} = \frac{1}{\pi\hbar} \int DOM(E)(E-\mu)T \frac{\partial f_{\rm FD}^0}{\partial T} dE$$
(1.9b)

The transmission coefficient, by its definition can be obtained by the mode-wise evaluation using the Fermi's golden rule, and can also be associated to the relaxation time or mean-free-path  $T = \langle \Lambda \rangle / L = 2 \langle v_x^2 \tau \rangle / \langle |v_x| \rangle$  (=  $4v\tau/3L$  in 3D). Using the Landauer formalism, anisotropic properties can be treated directly by summing the projection of transmission in the direction of interest. Also, the information of dispersion and of scattering are separated in the DOM and transmittance terms respectively, so that the contribution to transport of dispersion vs. scattering can be illustrated by comparing with the ballistic thermal conductance (setting T = 1). The transmission coefficient also provides a direct measure of the difference in energy and momentum relaxation process, where the transmission coefficient in the energy transport is larger indicating the probability of for a carrier reaching the other contact with its energy level uninterrupted is higher.

#### 1.1.4 Thermoelectrics in Landauer formalism

Thermoelectric effects include the followings: an electrical potential difference is created over a conductor under temperature difference, called the Seebeck effect and can be used to generate electricity between a temperature difference. An electrical current carries thermal energy and enables a heat flow, called Peltier effect and can be used for electrical cooling. The Thomson effect is the additional heat production rate when a current flowing under a temperature gradient. (Rowe, 2006)

The framework of Landauer formalism (Imry & Landauer, 1999; Lundstrom & Jeong, 2013) gives a clear picture of thermoelectric transport. Thermoelectric effect is a coupled transport process of electrical charge and thermal energy, driven under temperature and electrical potential gradients. The gradient of Fermi function is,

$$\frac{\partial f_0}{\partial x} = -\frac{\partial f_0}{\partial E} \frac{\mathrm{d}\mu}{\mathrm{d}x} - \frac{E - \mu}{T} \frac{\partial f_0}{\partial E} \frac{\mathrm{d}T}{\mathrm{d}x}$$
(1.10)

and the charge current density  $j_e$  and thermal current density  $j_Q$  can be expressed as follows.

$$j_{e} = -\frac{L}{A} \frac{e}{\pi \hbar} \int DOM(E) \mathcal{T} \left( \frac{1}{e} \frac{d\mu}{dx} + \frac{E-\mu}{T} \frac{dT}{dx} \right) \frac{\partial f_{0}}{\partial E} dE$$

$$= \mathcal{L}_{11} \left( -\frac{d\mu}{dx} \right) + \mathcal{L}_{12} \left( -\frac{dT}{dx} \right)$$
(1.11a)
$$j_{Q} = -\frac{L}{A} \frac{k_{B}T}{\pi \hbar} \int DOM(E) \mathcal{T} \left( \frac{E-\mu}{k_{B}T} \right) \left( \frac{d\mu}{dx} + \frac{E-\mu}{T} \frac{dT}{dx} \right) \frac{\partial f_{0}}{\partial E} dE$$

$$= \mathcal{L}_{21} \left( -\frac{d\mu}{dx} \right) + \mathcal{L}_{22} \left( -\frac{dT}{dx} \right)$$
(1.11b)

By definition, the electrical conductivity  $\sigma = \mathcal{L}_{11}$ . The Seebeck coefficient, the ratio of open circuit thermoelectric voltage,  $S = \frac{\mathcal{L}_{12}}{\mathcal{L}_{11}} = -\frac{d\mu}{dx} / \frac{dT}{dx}$ . The Peltier coefficient, the ratio of the heat flow and the electrical current is associate to,  $\Pi = \frac{\mathcal{L}_{21}}{\mathcal{L}_{11}}$ . The detailed balance in near-

equilibrium thermodynamics proves  $\mathcal{L}_{21} = \mathcal{L}_{12}T$ , i.e., Onsager reciprocal relation, which is exactly the Kelvin relation  $\Pi = ST$ . The coefficient of temperature driven thermal current  $\mathcal{L}_{22} = \kappa_{e}$  is electrical thermal conductivity (with uniform chemical potential), which is consistent with Eq. 1.9b by algebraic substitution. Also notice the when there is both current and temperature gradient in the channel, Eq. 1.11 can be substituted into  $j_{Q} = \frac{\mathcal{L}_{21}}{\mathcal{L}_{11}}j_{e} + \left(\mathcal{L}_{22} - \frac{\mathcal{L}_{12}\mathcal{L}_{21}}{\mathcal{L}_{11}}\right)\left(-\frac{dT}{dx}\right)$  thus  $\kappa_{e} = \mathcal{L}_{22} - \frac{\mathcal{L}_{12}\mathcal{L}_{21}}{\mathcal{L}_{11}} = \mathcal{L}_{22} - S^{2}\sigma T$  is alternatively defined as the electron thermal conductivity to avoid double-counting. The treatment expanded to two-band(Sivan & Imry, 1986) also gives an additional cross term  $\frac{\sigma_{1}\sigma_{2}}{\sigma_{1}+\sigma_{2}}(S_{1}+S_{2})^{2}T$  which is the bipolar diffusion term to be discussed in Section 2.2.

The charge and thermal current can be written in Landauer formalism and the Seebeck coefficient is thus written as Eq. 1.11.

$$S = \frac{\mathcal{L}_{12}}{\mathcal{L}_{11}} = \frac{-\frac{e}{\pi\hbar}\int DOM(E)\mathcal{T}\frac{E-\mu}{T}\frac{\partial f}{\partial E}dE}{\frac{e^2}{\pi\hbar}\int DOM(E)\mathcal{T}\frac{\partial f}{\partial E}dE}$$
(1.12)

Notice that the detailed parameters of the band structure, such as the effective mass, group velocity, degeneracies, etc. are canceled out in evaluating the ratio. As a result, the Seebeck coefficient only depends the form of the dispersion, i.e. depending on dimensionality and parabolic/linear dispersion. (Jeong, et al., 2010; R. Kim, Datta, & Lundstrom, 2009) In fact, the Seebeck coefficient vs. normalized Fermi level ( $\eta_F = (E_F - E_c)/k_BT$ ) all the non-degenerated semiconductor materials fall on the same curve, since they are all the three-dimensional parabolic band electrons.

#### 1.2 Thermal Conductivity Measurement for Solid-State Thin Films

Thermal characterization for micro/nanoscale materials and structures is generally challenging. Both the size of the material/structure and of the physical processes need to be considered when designing the heat source and the probe. The timescale of the physical processes is also critical in transient measurement methods. Additionally, for in-plane thermal conductivity measurement of thin-film or two-dimensional (2D) materials, extra heat sink or heat transfer channels should be avoided for sufficient sensitivity.

Several typical temperature transducers are developed for the small scale. Platinum resistance is widely used due to its high linearity and stability over a wide range of temperature, and compatibility with nanofabrication processes.(Kim, et al., 2001; Shi et al., 2003) The temperature resolution can be as pushed to 50 µK (Sadat, Meyhofer, & Reddy, 2012, 2013; Zheng, et al., 2013) and spatial resolution can be submicron depending on the fabricated structure. On the other hand, optical methods allowed non-contact thermal measurements. The thermal radiation spectrum is related to the temperature per Planck's law and thus infrared camera effectively maps the temperature with resolution of a few microns. Laser-based method brings the spatial resolution to sub-micron (diffraction limit of the light) when the temperature coefficients of e.g., reflectance (Cahill, 2004), peak shift and width of Raman scattering (Luo et al., 2014), etc. are calibrated to serve as thermal transducers. The spatial resolution can be improved to 10s of nanometers by tipbased methods e.g., scanning thermal microscope (Majumdar, 1999) and tip-enhanced Raman thermometry(Kumar, et al., 2015). Some electron properties are also sensitive to temperature that allow temperature measurements using an electron microscope, including its brightness(Khan et al., 2018; Yuan et al., 2020) and the electron energy loss spectroscopy (EELS) (Mecklenburg et al., 2015).

Electro-thermal micro-bridge is a typical method for thermal conductivities of thin films or nanowires (Shi et al., 2003). As showed in Figure 1.4(a), the sample film is suspended over the substrate patterned into two islands to eliminate undesired heat dissipation. All the heat transfer from one island to the other goes through the sample film. Platinum wires are fabricated on the islands as Joule heaters and resistive thermometers. The thermal conductance can be extracted from the measured temperature difference and heat flow rate. The method is reliable, well-standardized, and easily coupled to other experimental conditions like varied temperatures and a magnetic field. However, it's sensitive to the thermal contact, and the sample preparation takes much effort.

Micro-Raman thermometry method is a non-contact optical method, emerged with the discovery of graphene (Balandin et al., 2008). The sample is suspended on a hole or a trench of the substrate as the heat sink. A laser is focused at the center of the suspension region, serves as an optical heater, and induces Raman scattering at the same time. The heating rate can be obtained by optical absorption measurement and the Raman signal can be calibrated as the temperature transducer. The thermal conductivity is extracted via heat conduction modeling. The heat source

and the temperature measurement he Raman thermometry method requires minimal fabrication and sample preparation and was widely used in two-dimensional (2D) materials studies (Balandin et al., 2008; Cai et al., 2010; Huang et al., 2020a; Luo et al., 2015; Yan et al, 2014; Zhou et al., 2014)



Figure 1.4 In-plane thermal conductivity method for thin films. (a) SEM image of the electrothermal micro-bridge device. Reprinted from (Shi et al., 2003) (b) Schematic of micro-Raman thermometry method.

The uncertainty control of both steady-state methods above depends highly on the temperature calibration and heat transfer rate evaluation. Transient/frequency domain methods extract the thermal diffusion coefficient from the timescale signatures of the relative changes and do not require absolute values. Examples are, electro-thermal based Angstrom/3- $\omega$  method (Cahill, 1990; Vandersande & Pohl, 1980), laser-based time-domain thermal reflectance (TDTR) (Cahill, 2004) etc. The Raman thermometry can also be implemented in the time-domain using pulsed lasers for versatility. Using dual-wavelength for heating and probing, and varied chopping frequencies of the laser pulses, in-plane thermal conductivity can be extracted from supported sample films and without temperature and power calibration (Li et al., 2017; Wang et al., 2018, 2020).

#### 1.3 Topological Materials and Topological Surface States

Topological materials are an emerging category of matter named after its non-trivial topological order parameters. Topological surface states (TSS) are a new type of electronic states, distinctive from the ordinary electrons, supported on the surface of three-dimensional topological insulators (3D TIs). The introduction of the relevant concepts are mostly based on Refs (Hasan & Kane, 2010; Moore, 2010)

The paradigm to categorize and discover phases of matter is the central topic in condensed matter physics. Symmetries, remarked by the Landau's explanation of superfluidity using spontaneous symmetry breaking, has been successfully used to understand and characterize the matter phases or states. The study of the quantum Hall effect (QHE) led to an additional framework based on the topological order. The origin of the quantum Hall effect does not break any symmetry but instead defines new electron states. The quantum Hall states are insensitive to smooth change of material parameters and only accessible via quantum phase transitions. The insensitivity of continuous change is described by topology and the generalized (not limited to electron) states possessing this property are called topological states.

The behavior of TSS can be introduced from the edge and bulk states in QHE. The magnetic field *B* deflects the electrons from an electrical current by Lorentz force and leads to a voltage in the traverse direction as shown in Figure 1.5(a). This effect is called Hall effect and can be characterized by the Hall resistance  $R_{\rm H} = V_{\rm H}/I = B/e\rho_e$  defined by the ratio of the traverse Hall voltage  $V_{\rm H}$  and the current *I* and increasing linearly with the magnetic field. When the electrons are confined in a two-dimension (2D) system and experience low scattering rate (i.e. high purity and low temperature) and high magnetic field, the strong magnetic field localizes the electrons in cyclotron orbits and leads to energy levels called Landau levels (the energy of n<sup>th</sup> Landau level  $E_{\rm L}(n) = \hbar\omega_{\rm c}(n + \frac{1}{2})$ , where the cyclotron frequency  $\omega_{\rm c} = eB/m_{\rm e}$ ) that overrides the intrinsic band structure. The current now drifts the cyclotron orbits causing the Hall voltage, and the Hall resistance reaches to plateaus  $R_{\rm H} = h/\nu e^2$ , where  $\nu$  is the number of filled Landau level. The cyclotron motion of localized electrons makes the group velocity near zero and the bulk states are thus insulating. However, the electrons at the edge bounce back from the boundary and skip forward, so that the edge states serve as the conducting channel (Figure 1.5(d)).



Figure 1.5 Hall effects and topological phase. (a) Hall effect, (b) anomalous Hall effect and (c) spin Hall effect. (d) Cyclotron motion of localized QHE states in the bulk and skipping states at the topological-trivial interface. (e) Helical edge states with opposite spin polarizations supported at the rim of a QSHE system/2D TI.

Besides the magnetic field, electrons under the external electric field can also acquire a traverse group velocity when there is magnetization, spin-orbit coupling (SOC), etc. The additional velocity is generically formulated to be related to the change of phase of the Bloch wave when the external electrical field drives them to evolve in the momentum space. The process requires a spin-dependent scattering with the impurities or band structure, and the traverse motion of electrons is thus spin-dependent. In ferromagnetic materials, there are both an electrical potential difference and a spin potential difference across the channel proportional to the magnetization, called the anomalous Hall effect (AHE, Figure 1.5(b)). While the spin Hall effect (SHE) can be considered as the superposition of two AHEs with opposite spin chirality (Figure 1.5(c)). Thus, only spin potential difference, void of electrical voltage, exists across the channel and is proportional to spin-orbit coupling intensity.

The quantum spin Hall effect (QSHE) is the spin version of QHE or the quantized SHE with strong spin-orbit coupling. It is proved in the Haldane model that the QHE can be realized in periodic magnetic flux (with zero net external magnetic field) and the periodic magnetic flux can be replaced by the strong spin-orbit coupling. In a QSHE system, the bulk states are gapped and insulating, like conventional insulators and semiconductors. Spin-dependent edge states are supported around the boundary. Electrons with opposite spins counter-flow and form a pair of helical edge states. The strict correspondence of the spin polarization and the moving direction is called spin-momentum locking. The edge states are robust against disorders because the backscattering to the other state is prohibited per Fermi's golden rule, since the time-reversal symmetry is preserved. The Berry curvature of the Bloch wave, which is also effectively the generalization of the magnetic vector potential in terms of the Bloch Hamiltonian, is used to express the spin-dependent band structure. The integral of the Berry curvature over the momentum space is an integer and called the Chern number and the Chern number characterizes the topological order. Similarly in the QHE case, the Chern number obtained by integrating the magnetic vector potential is the occupied Landau level that also characterizes its topological order. This procedure can be visualized by taking the integral geometric curvature to obtain the genus number in spatial geometry and that the genus number is insensitive to the smooth deformation of the surface, i.e., the topology geometry. Thus, the 2D systems supporting QSHE, neglecting some subtlety, are called 2D topological insulators, and CdTe/HgTe/CdTe quantum well is the first proved instance.

The QHE is limited to 2D systems. However, QSHE can be generalized to 3D when the total Berry flux in the momentum space resembles a Dirac magnetic monopole which is not achievable for external magnetic fields. The TSSs in 3D TIs can be understood under the bulk-boundary correspondence in the field theory. The interior of 3D TIs is gapped with conduction/valence band like conventional insulators/ semiconductors. At its interface to vacuum (or states with a different topological order), i.e., its surface, the conductive TSSs emerge. Resembling the edge states in QSHE, TSSs are in-plane spin-polarized and the electron spin is locked to its momentum. Precisely, the spin, momentum, and surface norm are orthogonal. Time reversal symmetry is also preserved in 3D TIs. An electron scattering directly from a TSS to the opposite state is prohibited but its momentum can still be flipped indirectly via other states at the surface, thus the backscattering is suppressed but not prevented. Bi-Sb alloy is the first evidence

of 3D TIs. The TI material studied mostly in this thesis is the tetradymite family, i.e., Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, etc. It is well-known as one of the best room-temperature thermoelectric materials for decades and recently found a 3D-TI with a single Dirac cone of the TSS at Gamma point (the center of the Brillouin zone). The Dirac cone (Figure 1.6(a)) indicates the electrons with gapless and linear dispersion relation. The metallic and near-massless behavior of the electrons (often call Dirac fermions) resembles those in the Dirac cone in graphene, while spin-polarized and locked to the momentum instead. The bandgap is typically ~0.3 eV and the chemical potential can be tuned by their ternary/quinary compounds (e.g., Bi<sub>2</sub>Te<sub>2</sub>Se, BiSbTe<sub>3</sub>, BiSbTeSe<sub>2</sub>) deep into the bulk bandgap (Figure 1.6(b)) so that TSS-dominant transport properties can be realized in thin films even at room temperature.(Ren et al., 2010; Xu et al., 2014)

It is proposed that due to the proximity effect of the s-wave superconductor and the TSS, a peculiar electron behavior called Majorana fermions can be realized. The Majorana fermions are governed by non-abelian statistics and topologically protected from local decoherence, which makes a candidate for universal quantum computing. The TSS may also support an exotic magnetoelectric effect governed by axion equation (a postulated elementary particle model composing cold dark matters) instead of Maxwell equation, and thus TIs may serve as a solid-state experimental platform for particle physics theories. We are interested mostly in the transport properties that originated from its unconventional scattering mechanism. In section 2.2 we demonstrated that the TSS has unexpected large thermal conductance and Lorenz number, likely due to the scattering mechanism. The non-reciprocity, or more precisely spin-momentum locking of the TSS, also provides a switch to the transport. The spin polarization in TSS can be realized by transfer of spin torque from the magnetic substrate/contacts (Huang et al., 2017; Ojeda-Aristizabal et al., 2012; Shiomi et al., 2014; Tian et al., 2015), or optical spin injection (Kastl et al., 2015; McIver et al, 2011; Pan et al., 2017), i.e. using circularly polarized light with spin ±1 that selectively excited the topological states. The helicity-controlled transport of TSS by optical spin injection is mainly discussed in Chapter 3.



Figure 1.6 Topological surface states in 3D TIs. (a) The spin texture in the Dirac cone. (b) Band structure of Bi<sub>2</sub>Te<sub>2</sub>Se. The isolated solid lines representing TSSs, the blue shadows representing bulk conduction and valence bands.

#### 1.4 Objective and Scope

The objective of the dissertation is to measure the thermal transport properties of topological material thin-films and study the controlled transport behavior of the topological states. In Chapter 2, micro-Raman thermometry is applied to measure the in-plane thermal conductivity of 3D TI Bi<sub>2</sub>Te<sub>2</sub>Se and Weyl semiconductor trigonal tellurium thin films. The TSSs contribute much to the thermal conductivity in thin films and unexpected large Lorenz number is discovered for TSS electrons. The anisotropic thermal conductivity of tellurium was measured and explained by the phonon dispersion of the van der Waals stacking of spiral atomic chains. Chapter 3 shows the controlling of TSS using circularly polarized light. The circular photocurrent from the optical spin injection can be enhanced, suppressed, and inverted by electrical gating, and deeply broadened the field-effect photo-thermoelectricity. The photoconductivity under bias voltage is showed dependence with optical helicity with high fidelity and can be used as chirality detectors. Chapter 4 discusses future works on thermal conductivity tuning via controlled TSS and magneto-optic controlling and detection on TI-ferromagnetic structures.

## 2. MEASUREMENT OF THERMAL CONDUCTIVITIES IN THIN FILMS

In this chapter, micro-Raman thermometry is applied to measure the thermal conductivity of thin-film topological insulator Bi<sub>2</sub>Te<sub>2</sub>Se, and 2D tellurium (2D-Te) thin films. An unexpected rise of apparent thermal conductivity for thinner Bi<sub>2</sub>Te<sub>2</sub>Se films, contradicting to the classical size effect of ordinary thin films. The contribution of TSS to thermal and electrical conduction is extracted and leads to an unconventionally larger Lorenz number. Thermal conductivities of 2D-Te in all three axes are measured using micro-Raman thermometry and TDTR and the origin of the anisotropy is identified by first-principles calculation. This chapter is based on published works (Huang et al., 2020a; Huang et al, 2021a; Luo et al., 2018) with permission to reused the contents. Copyright © 2018 American Chemical Society, 2019 IOP Publishing Ltd., and 2021 Taylor & Francis Online.

#### 2.1 Introduction to micro-Raman thermometry

Optical properties of solids exhibit the electron behaviors and are generally sensitive to external parameters e.g., temperature, strain, etc. and vastly used as electronic structure analysis transducers for state parameters of solids (Prasankumar & and Taylor, 2012). Reflection/transmission spectroscopy illustrates the bandgap of insulators, absorbing for higher energy photons due to electron excitation and transparent for below-bandgap photons. Fourier-Transform infrared (FTIR) spectroscopy identifies the chemicals with their characteristic bond vibrational modes. The reflectance change of metals serves as a temperature transducer and widely used in thermal reflectance methods (experimental details of one example, TDTR, will be given in Section 2.3.1). Beyond the linear transmission/reflection process, the Raman effect, involving two photons, one absorbed and one emitted, provides additional information on the phonons (and quantized spin waves called magnons in ferromagnetic materials) in the solids.(Kittel & McEuen, 1996) The incident photon is inelastically scattered with a phonon (or magnon) created (Stokes process) or annihilated (anti-Stokes process), and result in a shift of the wavelength. The selection rules of the (first-order) Raman effect follow the energy and momentum conservation Eq. 2.1 (capital case for phonons, minuscule for photons). The classical scattering and quantum pictures
of Raman effect are illustrated in Figure 2.1, compared with the transitions in elastic scattering (Rayleigh effect) and infrared spectroscopy.



$$\omega = \omega' \pm \Omega; \mathbf{k} = \mathbf{k}' \pm \mathbf{K}$$
(2.1)

(e) Stokes (f) anti-Stokes (g) Rayleigh (h) infrared

Figure 2.1 Schematics of scattering in solids. Classical scattering pictures (a, b, c, d) and quantum transitions (e, f, g, h) in Stokes Raman scattering (a, e), anti-Stokes Raman scattering (b, f), Rayleigh scattering (c, g) and infrared phonon absorption (d, h), solid arrows for photons and dashed arrows for phonons.

In most cases, Raman spectroscopy is conducted with visible lasers and the maximum momentum exchange is 2k on the order of ~  $10^4$  cm<sup>-1</sup>, which is much smaller compared to a typical Brillouin zone ~  $10^7$ - $10^8$  cm<sup>-1</sup> (knowing the lattice constant of most materials < 1 nm). Thus, only the optical phonons at the Gamma point interact with light in a (first-order) Raman process. The energy of these phonons can be extracted from the Raman shifts, typically in the THz range (or 10-1000 cm<sup>-1</sup>). More information on the phonon dispersion can be obtained with higher power

density or photon energy. Higher-order inelastic scattering involving more than one phonon creation/annihilation (called Brillouin scattering) or the Raman effect excited by X-ray (inelastic X-ray scattering, IXS) are established methods to illustrate the momentum-dependence of phonon excitations.

A typical (Stokes) Raman spectrum, taking in Bi<sub>2</sub>Te<sub>2</sub>Se (Section 2.2) for example is shown in Figure 2.2. Each peak represents a phonon mode with its distinct vibrational pattern, named after a nonreducible representation of the lattice symmetry group.(Dresselhaus, Dresselhaus, & Jorio, 2008) A, B are associated with singly degenerated representations, E for doubly, and T for triply. The subscript numbers denote the ordinals of base function, and the letter denotes its parity (g for gerade means even parity in German, and u for ungerade meaning odd). The superscript denotes the ordinals of vibration patterns under the same representation. The group representations describe the additional selection rules governed by its symmetry.(Dresselhaus, Dresselhaus, & Jorio, 2008) The physical meaning is that the allowed electrical dipole excitations are determined by the symmetries of the lattice vibration excitation Hamiltonians. For example, the parity symmetry requires the final states of Raman process to be even, thus all the Raman active phonon modes are subscripted with "g", and the "u"-subscripted phonon modes are only active in the complementary infrared absorption spectrum for the same reason. The anisotropy (e.g., in black phosphorus (Luo et al., 2015)) and chirality (e.g., in 1-T phase MoS<sub>2</sub> (Chen et al., 2015)) of the lattice also exhibit symmetry-induced selective absorption/scattering depending on the light polarization.



Figure 2.2 Raman spectrum and corresponding phonon modes of Bi<sub>2</sub>Te<sub>2</sub>Se.

The Raman thermometry can be realized using the following three as the temperature transducer, the peak shift, the peak linewidth broadening, and the ratio of anti-Stokes/Stokes peak intensities.(Perkowitz, 1993; Prasankumar & Taylor, 2012) The temperature dependence of the Raman signal in silicon is shown in Figure 2.3(Hart, Aggarwal, & Lax, 1970) as an example. The probed phonon frequency decreases, the peak broadens, and the ratio of anti-Stokes/Stokes peak intensities increases, against the temperature increase. The peak shift is due to thermal strain and the altered phonon scattering which elongate and soften the covalent bonding, causing the redshift of the Stokes peaks. An ideal Raman peak is Lorentzian per Heisenberg's uncertainty principle  $\Delta\omega\Delta t \geq \frac{1}{2}$ , depending on the finite phonon lifetime. (In this thesis, here is the only case  $\Delta\omega$ standing for frequency broadening.  $\Delta \omega$  is used for peak shift below.) The phonon lifetime reduces as the scattering rate increases at a higher temperature so that the linewidth broadens. The ratio of anti-Stokes/Stokes peak intensities increases with temperature because the scattering rate of anti-Stokes/Stokes increases/decreases with the phonon population. The formalism for the temperature dependence of these transducers can be obtained from the statistics and scattering mechanisms of phonons, while empirical it is linear to the temperature within a small range since it's a small perturbation of the lattice. In all the cases reported in this chapter, the peak shift is used as the temperature transducer for the sensitivity and convenience of implementation. The Raman thermometry based on peak shift has been widely used in low-dimensional material thermal characterizations.(Balandin et al., 2008; Cai et al., 2010; Huang et al., 2009; Liu, Wu, & Ren, 2011; Luo et al., 2014, 2015; Peimyoo et al., 2015; Soini et al., 2010; Wang et al., 2012; Yan et al., 2014; Zhou et al., 2014)

The micro-Raman system used for this research is a commercial system Horiba LabRAM HR800 spectrometer coupled to an Olympus BX40 microscope, using a 632.8-nm He-Ne laser or a 532-nm Nd:YAG laser for excitation as shown in Figure 2.4. Edge filters are used to eliminate the Rayleigh signal so only Stokes signal can be obtained. The spectrum obtained by a dispersive grating onto a charge-coupled devices (CCD) array. The spectrum resolution with the 1800 grooves/mm grating is 0.27 cm<sup>-1</sup>. The incident laser power to the sample is controlled by the variable neutral-density (ND) filters. The beam-splitter (BS) and the power meter can also be installed as shown into the system for in-situ reflection/transmission measurements. A polarizer can also be placed at the entrance of the spectrometer (not shown) as an analyzer for polarized Raman spectrum studies.



Figure 2.3 Raman spectra of silicon at varied temperatures. Reprinted with permission from (Hart et al., 1970), Copyright (1970) American Physical Society



Figure 2.4 Raman spectrometer system and reflection/transmission measurement.

The Raman thermometry is calibrated on a Linkham THMS720 cryostat. The cryostat is equipped with a replaceable window allowing optical measurement and the combination of electrical heater and liquid nitrogen (LN<sub>2</sub>) supply allowed a wide range from -196 - 600 °C. For room-temperature thermal conductivity measurement reported in this chapter, the Raman

thermometry is calibrated within 20 - 80 °C and the peak shift is chosen as the temperature transducer due to its higher sensitivity and linearity. The temperature resolution depends on the temperature coefficient  $\chi_T$  (typically on the order of 0.01 cm<sup>-1</sup>/K) and the uncertainty from the peak fitting (~0.01-0.03 cm<sup>-1</sup>) so the temperature resolution is on the order of 1 K. A minimal incident power to obtain the temperature resolution (typically tens of microwatts) is used during temperature calibration.

The temperature obtained from Raman thermometry is named the Raman temperature  $\theta_{\text{Raman}}$ , which is an averaged temperature weighted per the Gaussian beam waist width  $w_0$  (and  $l_0$  for elliptical beam, obtained using standard knife-edge method) and absorption coefficient ( $\alpha$ ) as defined in Eq. 2.2. For the cases studied in this thesis, the films are sufficiently thin that the z-axis temperature difference is negligible so the z-axis weighting can be simplified as uniform and only 2D integral is used.

$$\theta_{\text{Raman}} = \frac{\int \theta(x, y, z) \exp\left(-\frac{2x^2}{w_0^2} - \frac{2y^2}{l_0^2}\right) \exp\left(-\frac{\alpha}{z}\right) dx dy dz}{\int_0^\infty \exp\left(-\frac{2x^2}{w_0^2} - \frac{2y^2}{l_0^2}\right) \exp\left(-\frac{\alpha}{z}\right) dx dy dz}$$
(2.2)

The thin film sample is suspended over a trench or through-hole (Figure 1.4(b)) the laser is focused at the center of the suspended region serving both the heat source and the thermometer. In most cases the suspension (even a vacuum ambient) is required, making sure the majority of the heat flowing through the sample film and draining at the heat sink, to obtain higher sensitivity (Cai et al., 2010; Luo et al., 2014). The heating power *q* is determined by laser absorption  $P_A$ ,  $q = P_A =$  $AP_i$ , where incident power  $P_i$ , absorption *A* (e.g., by measuring reflectance R and transmittance *T*). A heat conduction model with laser heating is used to calculate the temperature distribution under the Gaussian laser heat source, as given in Eq. 2.3. The heat loss to the air can also be accounted for by the heat conduction because the free convection boundary layer is much thicker (more than a few millimeters) than the heated region. The thermal conductivity is extracted from a heat conduction model (accounting for the shape factor *S* for the complex geometry, Eq. 2.4a). With the parameters measured and Raman thermometer calibrated, the thermal conductivity is measured by the regression of Raman shift vs. laser power (Eq. 2.4b).

$$\frac{\partial}{\partial x} \left( \kappa_x \frac{\partial \theta}{\partial x} \right) + \frac{\partial}{\partial y} \left( \kappa_y \frac{\partial \theta}{\partial y} \right) + \frac{\partial}{\partial z} \left( \kappa_z \frac{\partial \theta}{\partial z} \right) + \dot{q} = 0$$
(2.3a)

$$\dot{q} = \frac{AP_i}{\pi w_0 l_0 t} e^{-\left(\frac{2w^2}{w_0^2} + \frac{2l^2}{l_0^2}\right)} e^{-\frac{\alpha}{z}}$$
(2.3b)

$$q = S\kappa(\theta_{\text{Raman}} - \theta_{sink}) \tag{2.4a}$$

$$\kappa = \frac{\Delta q}{S\Delta\theta_{\text{Raman}}} = \frac{\chi_T A}{S} \frac{\Delta P_i}{\Delta \omega}$$
(2.4b)

### 2.2 Enhanced Thermal Conductivity of Bi<sub>2</sub>Te<sub>2</sub>Se thin films: Large Lorenz Number

Tetradymites has been intriguing for decades due to their thermoelectric performance at room temperature. (Venkatasubramanian, Siivola, Colpitts, & O'Quinn, 2001) Tetradymites were later identified as 3D TI (Zhang et al., 2009) and abundant following efforts were devoted to improving the bulk phase resistivity and achieving higher TSS contribution by alloying or ion doping(Ren et al., 2010; Wang et al., 2012; Xu et al., 2014). The special scattering mechanism is unprecedented from the thermal perspective and esp. the back-scattering suppression may lead to large electronic thermal conductivity even at a lower carrier density. Bi<sub>2</sub>Te<sub>2</sub>Se is selected for the thermal conductivity study due to its low bulk-electron contribution and high-quality lattice in which the quality of Raman signal is sufficient allowing thermal conductivity measurement. The bulk single crystalline Bi<sub>2</sub>Te<sub>2</sub>Se is grown by Dr. Ireneusz Miotkowski using the Bridgman-Stockbarger method, involving a melting process of the polycrystalline and seeded-growth during a slow cooling process. Single-crystalline tetradymites is layer-structured, atomic quintuples layers (QL, each layer composing of five sublayers of atoms, ~1-nm thick) bonded by van der Waals (vdW) force, as shown in Figure 2.5(a) (Ren et al., 2010), which can also be exfoliated like other 2D materials.(Teweldebrhan, Goyal, & Balandin, 2010). The band structure obtained by the angular-resolved photo-emission spectroscopy (ARPES) is shown in Figure 2.5(b) (Cao et al., 2014). The linear bands are the TSS and the brighter camelback band is the valence band. The conduction band of the pristine Bi<sub>2</sub>Te<sub>2</sub>Se is unoccupied thus dark.

## 2.2.1 Evaluating TSS Contribution to Thermal and Electrical Transport

The thin films of Bi<sub>2</sub>Te<sub>2</sub>Se are exfoliated with Nitto tapes (Nitto Denko. BT-150) from the Bridgman-grown bulk material. The exfoliated thin films were subsequently suspended on holey SiN membranes (Ted Pella #21535) using a wet transfer technique for Raman thermometry measurements (Details see Ref. Luo et al., 2015, and its Appendix 1). To unveil the role of surface states in the overall thermal transport in Bi<sub>2</sub>Te<sub>2</sub>Se, extensive efforts were put forward to bring the thickness down to 8 nm in order to reduce the bulk contribution as much as possible. In the Raman thermometry measurements, the suspended Bi<sub>2</sub>Te<sub>2</sub>Se films were heated by a He-Ne laser at various power. The temperature rise from laser heating was determined by the shift in the  $E_g^2$  Raman peak, and subsequently used in a 2D numerical heat transfer model to extract the in-plane thermal conductivity. Figure 2.6(a) shows Raman spectra and an optical image of a suspended 10-nm flake at elevated temperature. The  $E_g^2$  mode was used as the Raman thermometer for its good sensitivity to temperature change, with the temperature coefficient  $\chi_{Eg2} = -0.0113 \text{ cm}^{-1}/\text{K}$  (Figure 2.6(b)).



Figure 2.5 (a) Quintuple layered structure of Bi<sub>2</sub>Te<sub>2</sub>Se. Reprinted with permission from (Ren et al., 2010) Copyright (2010) by American Physical Society. (b) ARPES measurement of electronic band structure of Bi<sub>2</sub>Te<sub>2</sub>Se. Reprinted from (Cao et al., 2014) from arXiv.org.



Figure 2.6 Raman thermometer calibration of a 10-nm thick  $Bi_2Te_2Se$  film. (a) Raman spectrum of the film. Left inset: typical Raman spectra of the  $E_g^2$  mode at various temperatures. Right inset: optical image of the transferred film, scale bar: 5 µm. (b)  $E_g^2$  mode Raman shift vs. temperature. Dashed line is linear fit, whose slope is the temperature coefficient.

The measurements were carried out near room temperature (300 K) and the results are shown in Figure 2.7(a). The reported thermal conductivity measurements are performed by Dr. Zhe Luo. As the thicknesses of the Bi<sub>2</sub>Te<sub>2</sub>Se films decrease to less than 20 nm, the measured effective in-plane thermal conductivity  $\kappa$  undergoes a rapid increase from ~1 W/m·K to ~ 3 W/m·K for films less than 10-nm thick, indicating the possible contributions from surface carriers. Meanwhile, electrical transport measurements were conducted on a number of Bi<sub>2</sub>Te<sub>2</sub>Se devices with different thicknesses. For these electrical transport measurements, Bi<sub>2</sub>Te<sub>2</sub>Se flakes were exfoliated on a Si wafer with 300-nm thermally grown SiO<sub>2</sub> on top. Four Cr/Au electrodes were patterned using electron beam lithography (EBL) and standard lift-off processes, and four-probe sheet resistance  $R_S$  measurements were carried out (Figure 2.7 (b) inset). Figure 2.7 (b) shows the thickness-dependent effective 3D electrical conductivity  $\sigma = 1/(R_S t)$  measured at room temperature where t is the film thickness. As seen in Figure 2.7 (b),  $\sigma$  also has an uprising trend when the thickness is less than ~20 nm, similar to the thermal conductivity data in Figure 2.7 (a).



Figure 2.7 Thermal and electrical transport of  $Bi_2Te_2Se$  thin films. (a) The thickness dependence of the effective in-plane thermal conductivity  $\kappa$  measured by the Raman thermometry. (b) Effective 3D electrical conductivity  $\sigma$ . The relative uncertainty of data is  $\pm 2.5\%$ . All measurements are made at room temperature. Inset: optical graph of a typical device.

The higher effective 3D electrical conductivity at smaller thicknesses in  $Bi_2Te_2Se$  films can be attributed to the increase of TSS contribution due to the reduced bulk conduction.(Cao et al., 2014) Generally in TIs, the topological surface state gives a metallic conducting layer at the surface of the TI, while the bulk interior can be much less conducting if its carrier density (doping) is low. Furthermore, the surface state electrons can have high mobility (Cao et al., 2014; Ren et al., 2010) (~ 2000 cm<sup>2</sup>/Vs at low T and ~ 500 cm<sup>2</sup>/Vs at room T for our samples) and weak electronphonon coupling with the insulating bulk (Pan et al., 2012; Zhu et al., 2011).

To confirm the contribution of TSS to electrical conduction in the thin samples, we have systematically studied the electrical field and Hall effects of the Bi<sub>2</sub>Te<sub>2</sub>Se samples at various thicknesses. The electrical and magneto transport measurements are done by Dr. Jifa Tian. Details can be found in Ref. (Luo et al., 2018) and only the key conclusions are summarized here. The sample sheet resistance and the Hall resistance (representing the carrier density) of all samples can be modulated by back gating and extracted by Hall effect, respectively. For thick Bi<sub>2</sub>Te<sub>2</sub>Se samples (> 30 nm), the 2D carrier density extracted from the Hall resistance  $R_{\rm H}$  (=1/*ne*) using a single-band model is on the order of 10<sup>14</sup> cm<sup>-2</sup>, demonstrating that the electrical transport is dominated by bulk (hole) carriers. When the sample thickness is below 20 nm,  $R_{\rm H}$  changes sign, indicating the carrier type changes from hole to electron as the thickness decreases. The extracted 2D carrier densities of the thin samples are ~ 1.0 × 10<sup>13</sup> cm<sup>-2</sup> (thus, 5 × 10<sup>12</sup> cm<sup>-2</sup> for one surface) which is ~10 times

smaller than that of the thick sample. From the ARPES results of Bi<sub>2</sub>Te<sub>2</sub>Se bulk crystals,(Cao et al., 2014) we know that when the Fermi level is located at the bottom of the conduction band, the carrier density on one surface is ~  $1.0 \times 10^{13}$  cm<sup>-2</sup>, which is two times higher than the carrier density (5 ×  $10^{12}$  cm<sup>-2</sup> for one surface) extracted from our thin samples. Therefore, the transport in our thin samples with a low carrier density are contributed more by the TSS. We further find that the room temperature 2D carrier density (~ $1.2 \times 10^{13}$  cm<sup>-2</sup>) of the 18-nm flake is only ~ 1.7 times higher than that measured at T = 1.6 K (~  $7.0 \times 10^{12}$  cm<sup>-2</sup>), whereas it is 5 times higher for a 50-nm thick sample. We further note that the Hall resistance of our thin samples shows nonlinearity We further rule out the possible contribution from the band-bending induced trivial surface states since they are derived from the bulk states and far away for the CNP (if such states were populated, we would expect to have a much higher carrier density exceeding ~  $1.0 \times 10^{13}$  cm<sup>-2</sup> per surface). Details of all electrical and magneto measurements can be found in (Luo et al., 2018)

To further quantify the contributions of surface states to electrical and thermal transport, we analyze the electrical conductivity and thermal conductivity data using a two-layer transport model accounting for the contributions from surface states and bulk. The total electrical conductance (G) and thermal conductance ( $\Gamma$ ) are approximated as:

$$G = G_{\text{surf}} + G_{\text{bulk}} = G_{\text{surf}} + \sigma_{\text{bulk}}t$$
(2.5a)

$$\Gamma = \Gamma_{\text{surf}} + \Gamma_{\text{bulk}} = \Gamma_{\text{surf}} + \kappa_{\text{bulk}} t \tag{2.5b}$$

The subscripts surf and bulk represent contributions from surface and bulk, respectively.  $G = \sigma t$  and  $\Gamma = \kappa t$  are sheet conductance for the entire film. Here underlies an assumption that the bulk thermal conductivity  $\kappa_{\text{bulk}}$  is independent of the thickness, which does not hold if the thickness is close to or smaller than the phonon/electron mean-free-path. It is noted for a similar material Bi<sub>2</sub>Te<sub>3</sub>, more than 80% of heat is carried by phonons with phonon mean free path shorter than 8 nm (Wang et al., 2013). As our films have thicknesses larger than 8 nm, it is expected the reduction of bulk thermal conductivity due to boundary scattering is small. However, if the reduction of bulk thermal conductivity due to a smaller mean-free-path in thin films is considered, an even higher surface contribution to the total thermal conductance will be obtained, which will be consistent with our main conclusions discussed below. An analysis of the effect of the reduction of bulk thermal (and electrical) conductivity is provided as follows. When the thin-film thickness approaches the bulk mean-free-path (MFP), surface scattering of the bulk charge/energy carriers can suppress transport. The large contribution of surface electrons to thermal transport shown

above is a prudent estimation since the bulk electron and phonon contribution considering the surface scattering can be even smaller. Here, we employ the expression of MFP of film  $\Lambda_f$  as  $1/\Lambda_f = 1/\Lambda + 1/\beta t$ , which will yield the expression of transmittance  $\Im_{ss} = t/(t+\Lambda/\beta)$  that is commonly used to estimate the effect of surface scattering (Kaiser et al., 2017; Majumdar, 1993). Here,  $\Im_{ss}$  represents the ratio of transport properties with and without surface scattering;  $\Lambda$  is the grey or lumped MFP of electrons (subscript e) or phonons (subscript ph); *t* is the characteristic length which is the thickness in this case,  $\beta$  is a parameter that represents the degree of scattering, which can be regarded as a simplification to more rigorous treatments of diffusive vs. specular surface scattering (McGaughey et al., 2011; Sondheimer, 2001). Eq. 2.6 are then rewritten as follows:

$$G = G_{\text{surf}} + G_{\text{bulk}} = G_{\text{surf}} + \frac{t^2}{t + \Lambda_e / \beta_e} \sigma_{\text{bulk}}$$
(2.6a)

$$\Gamma = \Gamma_{\text{surf}} + \Gamma_{\text{bulk}} = \Gamma_{\text{surf}} + \frac{t^2}{t + \Lambda_e/\beta_e} \kappa_{\text{bulk,e}} + \frac{t^2}{t + \Lambda_{ph}/\beta_{ph}} \kappa_{\text{ph}}$$
(2.6b)

There is no data of MFP of Bi<sub>2</sub>Te<sub>2</sub>Se materials in literature. Here we estimate the scattering effect using MFP of a similar material Bi<sub>2</sub>Te<sub>3</sub>. A mode-wise lattice thermal conductivity study of Bi<sub>2</sub>Te<sub>3</sub> using ab initio-MD showed that more than 80% of lattice thermal conductivity is contributed by phonons with MFP lower than 8 nm (Wang et al., 2013). For the bulk electron mean free path, we use  $\Lambda_e = 13$  nm of Bi<sub>2</sub>Te<sub>3</sub> from a first-principles-based calculation of conduction band/valance band MFP (Pettes et al., 2013). It is suggested that for thin films with diffusive boundaries,  $\beta_{ph}$  between 2.6~4.6 gives good approximation to the Boltzmann solution (Flik & Tien, 1990; Kaiser et al., 2017; Majumdar, 1993). We use the values  $\beta_e = \beta_{ph} = 3$  here as an estimation of the effect of diffusive scattering. This yields  $G_{surf} = 0.13 \text{ k}\Omega^{-1}$ ,  $\sigma_{bulk} = 6.0 \times 10^3 \text{ S/m}$ ,  $\Gamma_{surf} = 2.0 \times 10^{-8} \text{ W/K}$ ,  $\kappa_{bulk} = 0.94 \text{ W/m}\cdot\text{K}$ . Hence, the analysis considering the surface scattering also shows a large contribution of the surface state, and as expected, even larger than the result obtained using linear fitting (Eq. 2.5).

# 2.2.2 Violation of Wiedemann-Franz Law and Large Lorenz Number in Topological Surface States

The thickness-dependent total electrical and thermal (sheet) conductance calculated ( $G_s = \sigma t$ ,  $\Gamma_s = \kappa t$ ) from the experimental data ( $\sigma$  and  $\kappa$ ) are shown in Figure 2.8(a, b). The linear fit of both

data show a non-zero intercept, which is attributed to the surface conductance, and the slope is the bulk conductivity:  $G_{\text{surf}} = 0.11 \text{ k}\Omega^{-1}$ ,  $\sigma_{\text{bulk}} = 6.0 \times 10^3 \text{ S/m}$ ,  $\Gamma_{\text{surf}} = 1.4 \times 10^{-8} \text{ W/K}$ , and  $\kappa_{\text{bulk}} = 1.0 \text{ W/m}\cdot\text{K}$ . Figure 2.8(c) shows the surface electrical (thermal) conductance to the total electrical (thermal) conductance ratio,  $G_{\text{surf}}/G$  ( $\Gamma_{\text{surf}}/\Gamma$ ). As the thickness decreases, the contribution from the surface conductance rises up from less than 20% up to 60% for electrical conductance, and up to 70% for thermal conductance. The extracted room-temperature bulk electrical resistivity  $\rho = 1/\sigma \sim 0.017 \ \Omega \cdot \text{cm}$ , is comparable with the reported resistivity  $0.01-0.02 \ \Omega \cdot \text{cm}$  measured in thicker Bi<sub>2</sub>Te<sub>2</sub>Se bulk crystals (Ren et al., 2010). The bulk thermal conductivity value is also consistent with previously reported theoretical and experimental data of Bi<sub>2</sub>Te<sub>3</sub> (Goldsmid, 1956; Pettes et al., 2013; Qiu, Sun, & Ruan, 2011), which is of similar lattice structure as Bi<sub>2</sub>Te<sub>2</sub>Se. The results show that, at sufficiently small thickness, the electrical and thermal transport of thin Bi<sub>2</sub>Te<sub>2</sub>Se films are significantly influenced by the surface state, consistent with our field and Hall effects.

To compare the experimentally measured total thermal conductivity with the model prediction using either  $L_{surf}$  or  $L_0$ , the in-plane thermal conductivity is calculated using the following Eq. 2.7:

$$\kappa = \frac{\Gamma_{\text{surf}}}{t} + \kappa_{\text{bulk}} = \frac{LTG_{\text{surf}}}{t} + \kappa_{\text{bulk}}$$
(2.7)

We use both  $L_{surf}$  and the Sommerfeld value  $L_0$  in the calculation, and the calculated  $\kappa$  (using Equation 2.6, with  $G_{surf}$  and  $\kappa_{bulk}$  fitted above) values are shown as solid lines in Figure 2.8(d). The line calculated using  $L_{surf}$  fits the experimental data reasonably well, while the line using  $L_0$  cannot capture the significant thermal conductivity rise for thinner films. Note that we are not able to separate the contributions of bulk electrons and phonons in  $\Gamma$ , so the Lorenz number  $L_{bulk}$  for bulk electrons cannot be extracted.



Figure 2.8 Analyses of the transport properties of Bi<sub>2</sub>Te<sub>2</sub>Se thin films to extract surface and bulk contributions. (a) Electrical sheet conductance  $G_{tot}$  measured at  $V_g = 0V$  and a linear fit (dashed line). (b) Thermal sheet conductance  $\Gamma$  and linear fit. (c) Calculated ratio of surface electrical (thermal) conductance  $G_{surf}$  ( $\Gamma_{surf}$ ) to the total conductance G ( $\Gamma$ ). (d) Fitting the in-plane thermal conductivity *k* (experimental data from Figure 2.7(a)) using the extracted Lorenz number *L* and Sommerfeld value  $L_0$  in Eq. (2). The black pyramid symbol in (a), (b) and (d) represents the value obtained from a separate four-terminal Bi<sub>2</sub>Te<sub>2</sub>Se -SiN device.

An alternative way to estimate the Lorenz number without using the linear extrapolation is directly using the measured data for the thinnest films studied. We assume that for the measured thermal conductivity, the phonon contribution is 1 W/m-K, the value we measured for thicker films, and subtract this value from the measured thermal conductivity to obtain the thermal conductivity from charge carriers,  $\kappa_e$ . This will give us a lower bound of the Lorenz number since the phonon contribution is likely to be less for thin films. For the 8 nm-thick film, its  $\kappa_e$  and *G* values are 1.96 W/m-K and 0.16 1/k $\Omega$ . This will yield a Lorenz number of  $3.2 \times 10^{-7} \text{ V}^2/\text{K}^2$ , still significantly higher than the Sommerfeld value.

Including the MFP analysis yields  $L_{surf} = 5.0 \times 10^{-7} \text{ V}^2/\text{K}^2$ , or a 17% increase in  $L_{surf}$  compared with the estimation assuming no surface scattering or specular scattering (or  $\beta_e$  and  $\beta_{ph}$  approach infinity). Hence, the analysis considering the surface scattering also shows large enhancement of Lorenz number, and as expected, even larger than the result obtained using linear fitting (Eq. 2.5). It also occurs that a recent simulation showed the bulk accumulative thermal conductivity gets 80% for phonons with MFP lower than 20 nm. We also analyzed the data without the thinnest flake. As shown in Table 1 below, large surface Lorenz number can be extracted from any combination of these factors. The model with a larger MFP gives the result of a larger Lorenz number.

Table 2.1 Comparison of calculated Lorenz number

linear $(4.24 \pm 0.80) \times 10^{-7} \text{ V}^2/\text{K}^2$ $(4.04 \pm 0.93) \times 10^{-7} \text{ V}^2/\text{K}^2$	
MFP=8 nm $(4.99 \pm 0.89) \times 10^{-7} \text{ V}^2/\text{K}^2$ $(5.03 \pm 0.90) \times 10^{-7} \text{ V}^2/\text{K}^2$	
MFP~20 nm $(5.42 \pm 0.90) \times 10^{-7} \text{ V}^2/\text{K}^2$ $(5.48 \pm 0.87) \times 10^{-7} \text{ V}^2/\text{K}^2$	

There was a concern that the SiO<sub>2</sub> dielectric layer underneath the TI film used for the electrical measurements could alter the electronic properties of the TI films to be different from those suspended TI films (without such a SiO<sub>2</sub> substrate layer) in the thermal transport measurements, for example by shifting the Fermi level relative to the Dirac point (Chang et al., 2011; Jenkins et al., 2013). There was also a concern that the Bi<sub>2</sub>Te<sub>2</sub>Se device fabrication process for the electrical measurements could alter the quality of the Bi<sub>2</sub>Te<sub>2</sub>Se films. To check this, a four-probe device was first patterned on a SiN membrane (Ted Pella) with a 3-µm-diameter throughhole milled by FEI Quanta focused ion-beam (Figure 2.9), and then the Bi<sub>2</sub>Te<sub>2</sub>Se flake was transferred onto the probes. The same sample was then used for both thermal and electrical conductivity measurements at room temperature. Therefore, this flake did not go through any nanofabrication processes. The measurement results are shown as the black pyramid symbol in Figure 2.8(a, b, and d). It is seen that the measured electrical conductance and thermal conductivity are in good agreement with other experimental data, and they also lie in the vicinity of the model prediction using the large *L*<sub>surf</sub>.



Figure 2.9 SEM image of Pt contacts and optical image of suspended Bi<sub>2</sub>Te<sub>2</sub>Se device on SiN membrane (inset). Scale bar of the inset is 5 µm.

Now we discuss the possible reasons behind the large surface Lorenz number or the large Lorenz number for very thin films. The observed large surface Lorenz number  $L_{surf}$  can be attributed to several possible origins. One possible reason for the observed large Lorenz number is bipolar diffusion in semiconductor materials (Goldsmid, 2010). Wiedemann-Franz law is based on the single-band picture, so that when two or more bands contribute to transport, Wiedemann-Franz law can break down (Weathers et al., 2015). When both electrons and holes are thermally excited (for example, in non-degenerate semiconductors with small bandgap at room or elevated temperature) and a temperature difference is created, the carriers diffuse to the colder region. In addition to the sum of the thermal transport by electrons and holes separately, the carrier recombination at the colder side releases energy, which enhances the total thermal conductivity(Goldsmid, 1956; Yoshino & Murata, 2015). This can be the case for the zerobandgap, nearly charge-neutral surface states as the electrons and holes are readily excited thermally. Based on the Boltzmann transport equation, the electronic thermal conductivity  $\kappa_e$  can be written as(H. J. Goldsmid, 2010)

$$\kappa_{\rm e} = \kappa_{\rm n} + \kappa_{\rm p} + \frac{\sigma_{\rm n}\sigma_{\rm p}}{\sigma_{\rm n} + \sigma_{\rm p}} \left(S_{\rm n} + S_{\rm p}\right)^2 T \tag{2.8}$$

The third term comes from the bipolar diffusion which takes a maximum value when  $\sigma_n = \sigma_p$ , and it could be much larger than either  $\kappa_n$  and  $\kappa_p$ . Therefore, the bipolar contribution is in favor

of small bandgap (for high  $\sigma_n$  and  $\sigma_p$ ) as well as the Fermi level pinned around the neutrality point to achieve  $\sigma_n = \sigma_p$ . While enhancing heat transfer, bipolar diffusion does not increase electrical conductivity (meaning  $\sigma = \sigma_n + \sigma_p$ ), hence resulting in an increased Lorenz number. Experimentally, bi-polar effect enhanced electronic thermal conductivity was previously observed at elevated temperature in small-gap semiconductors such as Bi<sub>2</sub>Te<sub>3</sub> (Goldsmid, 1956), Al-based quasicrystals (Takeuchi, 2009), and  $In_4Se_{3-x}Te_x$  (Rhyee. et al., 2010). Further, first-principles calculations predict that a large increase of Lorenz number (up to 10 times the Sommerfeld value) can occur in  $Bi_2Te_3$  (Huang & Kaviany, 2008; Pettes et al., 2013) and skutterudites (Chaput et al., 2005) when the Fermi level sits near the charge neutral point (center of the bulk bandgap). Additionally, it has been predicted that the bipolar effect exists for Dirac electrons in graphene with a 1.8- to 4-fold increase of L at room temperature, or any systems with a zero band-gap and near charge neutrality condition (Yoshino & Murata, 2015). Our Bi<sub>2</sub>Te<sub>2</sub>Se thin films do have a small bulk bandgap measured to be ~0.3 eV (Cao et al., 2014) and gap-less TSS. Moreover, as discussed above, transport measurements indeed indicated that for thicknesses less than 20 nm, our samples were nearly charge neutral. Therefore, in our case, it is possible that the thermally populated surface electrons and holes are involved in the bipolar diffusion process that causes the observed large Lorenz number in our Bi<sub>2</sub>Te<sub>2</sub>Se thin films.

To illustrate the possible contributions from surface states and bipolar diffusion to transport processes, we utilize a simple electronic band model to calculate the transport properties (Figure 2.10) and provide some physical insight. The calculation is performed by Dr. Jesse Maassen. Our adopted band model for Bi<sub>2</sub>Te<sub>2</sub>Se, depicted in the inset of Figure 2.10(b), includes a 3D parabolic dispersion ( $E(k) = \hbar^2 k_{3D}^2/2m^*$ ) for the conduction and valence bands (bulk states) and a 2D linear dispersion ( $E(k) = \hbar v_F k_{2D}$ ) for the TSS band (surface states). The bulk bands are 3D, the number of states increases with film thickness, whereas the 2D surface bands have a constant number of states. Using this simple electronic band model, and assuming a constant mean-freepath for the surface and bulk states, we solve the Boltzmann transport equation within the Landauer approach (Jeong et al., 2010; Kayyalha et al., 2016) and extract the electronic conductivity, Seebeck coefficient, electronic thermal conductivity, and Lorenz number. Note that bipolar, or multiband, effects are included in the calculation. Figure 2.10(a) shows the calculated electrical sheet conductance (electrical conductivity times film thickness) versus film thickness. The total *G* scales linearly with thickness, as a thicker film increases the number of conducting bulk states. As the film thickness goes to zero, a constant contribution from the surface states remains. The thermal conductivity, presented in Figure 2.10(b), increases with decreasing film thickness, as the surface contribution becomes larger and dominates in the thinnest films. With thicker films the lattice contribution is dominant (the phonon contribution is approximately 0.85 W/m·K).



Figure 2.10 Calculated transport properties of Bi<sub>2</sub>Te<sub>2</sub>Se thin films with surface and bulk contributions. (a) Electrical sheet conductance *G* versus film thickness, with contributions from surface and bulk. (b) Thermal conductivity  $\kappa$  versus film thickness, with contributions from surface, bulk and lattice. (c) Ratio of surface electrical (thermal) conductance  $G_{\text{surf}}$  ( $\Gamma_{\text{surf}}$ ) to the total conductance *G* ( $\Gamma$ ). (d) Lorenz number versus film thickness, compared against the Sommerfeld value 2.44×10<sup>-8</sup> V<sup>2</sup>/K<sup>2</sup>.

Particularly, to illustrate the contribution of the surface states to the electrical and heat transport characteristics, Figure 2.10(c) shows the calculated  $G_{\text{surf}}/G$  and  $\Gamma_{\text{surf}}/\Gamma$ . As expected, the surface states play an important role in the thinnest films, when there are fewer bulk conduction channels.  $\Gamma_{\text{surf}}/\Gamma$  is smaller than  $G_{\text{surf}}/G$  in part because of the lattice contribution to thermal conductivity which increases  $\Gamma$ . The calculated Lorenz number, presented in Figure 2.10(d), is

found to be greater than the Sommerfeld value and shows a peak value of  $7 \times 10^{-8} \text{ V}^2/\text{K}^2$  for a 20 nm thickness. *L* is thickness dependent due to the relative contributions of surface versus bulk (including the bipolar diffusion) conduction, and exhibits a peak when both are roughly equal. The calculation also shows that the maximum *L* from the surface states alone is  $5.8 \times 10^{-8} \text{ V}^2/\text{K}^2$ , and the combination of both surface and bulk leads to an effective *L* that is greater than their individual components. This simple band model shows results consistent with experimentally observed trends and demonstrates a large contribution to transport from the surface states in the thinnest films. Differences between theory and experiment can result from the band model and the parameters used, for example, a thickness dependence of the Fermi level in the samples and the particular energy dependence of the dominant scattering mechanism and the mean-free-paths.

Another possibility is the effect of Dirac fluid of TSS electrons, with a strongly interacting electron-hole plasma formed near the Dirac point (Crossno et al., 2016; Principi & Vignale, 2015). The Dirac fluid theory suggests that in the temperature range where the electron-electron scattering is the dominating charge carrier scattering mechanism, the hydrodynamic nature of the charge carriers leads to the decoupling of charge and (electronic) heat current (Crossno et al., 2016; Lee et al., 2017; Principi & Vignale, 2015). In this case, the charge current is limited by the viscosity of Dirac fluid, while the heat current carried by electrons (holes) is limited only by impurity scattering. This will inevitably lead to the breakdown of the Wiedemann-Franz law, which has been theoretically predicted in graphene(Foster & Aleiner, 2009; Müller et al., 2008). Indeed, a nearly 20-fold increase of the Lorenz number over the Sommerfeld value was recently experimentally observed in graphene near 75 K (Crossno et al., 2016). In our case, as the sample thickness decreases from 80 nm to below 20 nm, the extracted carrier density decreases by more than one order of magnitude, and the transport in our thin samples is dominated by the TSS with its Fermi level near the CNP. Furthermore, the observed nonlinearity of the Hall resistance in the samples indicates the coexistence of electrons and holes. Thus, in our thin samples, the majority of electrical and/or thermal transport originates from both the electrons and holes near the CNP of TSS, where the coupling between electronic and heat currents due to the charge carrier (electron or hole) may be significantly weakened, which can lead to a large Lorenz number.

In summary of Section 2.2, the thickness-dependent in-plane thermal and electrical conductivity of Bi<sub>2</sub>Te<sub>2</sub>Se TI thin films was measured, and a large enhancement was observed when

the thickness is reduced to less than 20 nm. Moreover, a Lorenz number much larger than the Sommerfeld value for the TI surface was found. Possible mechanisms include the unique transport properties of surface states due to the electrical and thermal current decoupling in the Dirac fluid as well as bipolar diffusion of electrons and holes at TI surfaces. A simple computational model was employed to explain that the surface states and bipolar diffusion can indeed lead to enhanced electrical and thermal transport and large Lorenz number. Further work is needed to examine the detailed relative importance of these two mechanisms (or possible involvement of additional mechanisms) in the observed enhancement of the Lorenz number.

#### 2.3 Anisotropic Thermal Conductivity in Two-Dimensional Materials

The recently debuted two-dimensional Tellurium (2D-Te) was found to be a high-mobility, environmentally stable material for novel transistors(Du et al., 2017; Wang et al., 2018). 2D-Te has already shown engrossing bulk electronic properties of semiconducting (Bottom, 1952; von Klitzing & Landwehr, 1971), photo-response (Liu et al., 2010), thermoelectricity(Lin et al., 2016; Peng, Kioussis, & Snyder, 2014), and piezoelectricity(Royer & Dieulesaint, 1979). Its application in transistor was first studied after the substrate-free solution process of large-area high-quality 2D-Te was developed (Wang et al., 2018). A field-effect mobility value as high as 700 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at room temperature and a large ON-state current of 1 A mm<sup>-1</sup> were observed on pristine flakes (Wang et al., 2018), and even higher performance CMOS devices were soon realized (Qiu et al., 2018). The high mobility enables near/mid-infrared photodetectors with selective polarization (Amani et al., 2018; Deckoff-Jones et al., 2019; Shen et al., 2020; Tong et al., 2020). Competitive piezoelectric (Gao et al., 2017; Wang et al., 2020) and thermoelectric (Qiu et al., 2019) performances were also observed in 2D-Te devices that open the pathway to novel energy sources for wearable devices (Wang et al., 2020). It is also predicted that 2D-Te may exhibit multiple stable phases that support diverse potential applications (Xiang et al., 2019; Zhu et al., 2017).

The 2D-Te lattice is in the trigonal phase, the same as bulk Te. Each Te atom is covalently bonded to its two nearest neighbors in a trigonal helical chain, and individual chains are stacked together by the van der Waals (vdW) force (Figure 2.11(a)). For atomic-thin Te layers, firstprinciples modeling also predicted 2D-Te has stable  $\alpha/\beta/\gamma$ -phases (Zhu et al., 2017) with a distinctive lattice structure that enables varied electrical and thermal properties, while experimental results of these transport properties are yet reported. In the 2D-Te we studied, the helical chains are in-plane, and the lattice configuration is like a "bamboo raft". The anisotropic transport properties naturally arise from the anisotropic atomic structures and bonding in the plane. Although the dynamics of this van der Waals (vdW) stacking helical chain lattice drew attention quite early (Martin, Lucovsky, & Helliwell, 1976; Pine & Dresselhaus, 1971), its thermal conductivity of 2D-Te has never been reported, even rarely for the bulk. Thermal properties of annealed high-purity bulk tellurium were measured at the Thermophysical Properties Research Center, Purdue University in the 1970s, with room temperature thermal conductivity of 3.38 W/m·K in the c-axis (along-chain) and 1.97 W/m·K in the a-axis (across-chain) (Ho, Powell, & Liley, 1972). Thermal conductivity of polycrystalline tellurium was recently measured to be 1.6 W/m·K by the laser flash method (Lin et al., 2016). First-principles calculations showed tellurium lattice thermal conductivity can be as low as 2.77 (along-chain) and 1.22 (across-chain) W/m·K for (trigonal) bulk (Peng, Kioussis, & Stewart, 2015) and 4.08 (zig-zag) and 2.16 (armchair) W/m·K for a β-phase Te atomic layer (Gao, Tao, & Ren, 2018), which has a stiffer bounding, at room temperature.



Figure 2.11 Characterization of tellurene thin films. (a) Illustration of the lattice structure of 2D-Te. (b) Optical microscope (AFM) image of 2D-Te (30-nm thick) transferred onto Si trench-grids. Scale bar: 10 μm. (c) Identification of lattice axes by polarized Raman spectra. (d) Optical image of the laser line. Scale bar: 5 μm.

The 2D tellurium thin films studied in this work are grown through Na<sub>2</sub>TeO<sub>3</sub> reduction by N<sub>2</sub>H<sub>4</sub> in alkaline solution at elevated temperature (Wang et al., 2019, 2018), then assembled into a single-layer continuous thin film through the Langmuir-Blodgett (LB) process (Zasadzinski et al, 1994). The crystal growth is limited by the organic ligands PVP and only epitaxially extends in the kinetic-preferred lattice orientation. The solution-grown tellurium films hence usually have a trapezoid shape, in which the parallel edges are along the chain. This can be verified by polarized Raman spectroscopy (Luo et al., 2015; Wang et al., 2018): a polarizer is placed at the entrance aperture of the spectrometer with its transmission axis parallel to the incident laser polarization. The optical phonon modes are sensitive to the laser polarization due to the polarization selection rule arise from the lattice structure, and thus can be used to confirm the lattice orientation as shown in Figure 2.11(b) and the comprehensive polarization-resolved and thickness-dependent Raman spectroscopy is summarized in Figure 2.12. The vibration patterns of the Raman modes are also illustrated in Figure 2.11(b) inset.



Figure 2.12 Raman spectra of 2D-Te (a) Raman spectra for 2D-Te with different thickness. (b) Polarization-resolved Raman spectra of a 13.5-nm 2D-Te. (c-f) Fitting curves of the polarization dependent Raman shifts. Reprinted with permission from (Wang et al., 2018). Copyright (2018) by the Nature Publishing Group

The low adhesion of the 2D-Te thin film surface to the PMMA polymer leads to a very low yield of the PVA/PMMA wet-transfer method. Instead, the 2D-Te films are acquired on degreased

glass slides, then transferred onto the dry-etched silicon trenches (Figure 2.11(c)) using a capillaryassisted stamping method. The capillary force at the meniscus edge of the water-air-film interface provides additional adhesion that picks the film up and the weak adhesion between 2D-Te and PDMS allows dropping off onto Si substrates. The method is adapted from Ref. (Ma et al., 2017; Zhang, Liu, & Xu, 2017) and the details are also summarized in Appendix 1.

#### 2.3.1 Thermal Conductivity Measurements of 2D-Te

We transfer solution-synthesized 2D-Te of 15-200 nm thickness and suspend them on 5- $\mu$ m-wide silicon trenches to measure the in-plane thermal conductivity of 2D-Te using the micro-Raman method. Using the polarized Raman spectroscopy described above, all the 2D-Te flakes studied have <5° of its chain axis aligned to the trenches. Atomic force microscope mapping is conducted on multiple edges to obtain thickness and verify uniformity.

The temperature dependence of the peak shift of the A1 Raman mode is used as a microscale optical thermometer. The sample is first installed in a heating stage to calibrate the Raman peak shift ( $\omega$ ) vs. temperature ( $\theta$ ), excited with a 633-nm laser ~15  $\mu$ W to minimize the temperature rise. Both along-chain and across-chain directions are calibrated, and it is found that the A1 mode with cross-chain laser polarization offers the highest sensitivity, i.e., the largest Raman peak shift vs. temperature change (Figure 2.13(a)), and is thus chosen for the subsequent temperature measurements. The temperature coefficient  $\chi_T$  is specific to the mechanical condition in which the calibration is performed (i.e., suspended, stress-free due to thin shell buckling), and calibration and actual thermal transport measured are performed in the exact same condition (Luo et al., 2018). The reliability of this calibration issue is further addressed in Section 2.4.

All micro-Raman in-plane thermal conductivity measurements are performed at room temperature. A 50- $\mu$ m-wide slit is placed in the laser beam path to create a line-shape laser beam at the focal plane (Figure 2.11(d)). The laser intensity distributions are Gaussian in both directions, and the widths are characterized to be 0.98 and 9.6  $\mu$ m, respectively. The line-shaped laser beam is aligned to the center of the trench, creating a quasi-one-dimensional heat flow perpendicular to the trench in the suspended 2D-Te film. In this scenario, heat flow in the 2D-Te film is dominated by the conduction in one lattice orientation, isolating the anisotropic thermal conductivity.

The 2D-Te films presented in Figure 2.13 were obtained from the same batch of solution synthesis for consistency. This batch of samples were measured by Mauricio Segovia. We collect

a series of Raman spectra, which is then converted to the temperature rise using the calibrated  $\chi$ , with increasing incident laser power. A typical Raman shift versus incident laser power for a 35nm thick film is shown in Figure 2.13(b). The absorbed laser power is also needed for thermal conductivity extraction, and is measured for each individual film by measuring reflection, R and transmission, T. Since the transmission of the 2D-Te on Si-trenches cannot be measured, a separate batch of 2D-Te films with thicknesses in the same range are prepared on degreased glass slides and the absorptivity of 2D-Te films is then obtained by regression. We then obtain the relation between temperature rise versus absorbed power which is used to extract the thermal conductivity as described below.

The three-dimensional heat conduction model, Eq. 2.3(a), is used to extract in-plane thermal conductivity, even though heat flow is dominant along one direction by using a line-shape laser beam. The Gaussian laser heat source is given by Eq. 2.3(b). The measured temperature rise is a Gaussian-weighted average temperature per the laser focal line intensity distribution, per Eq. 2.2. In Eq. 2.2 and 2.3, the laser heating and the temperature in the z-direction are assumed to be uniform, due to the thickness being small comparing to the other two directions. The experimentally measured temperature rise versus absorbed power,  $d\theta_{Raman}/dP_A$ , is compared with the calculated slope to find the thermal conductivities.  $\kappa_{l'}$  and  $\kappa_{\pm}$  are extracted by an iterative procedure because the thermal conductivity along the trench also weakly affects the temperature rise due to the finite length of the line laser. The extracted in-plane thermal conductivities are presented in Figure 2.13(c, d), which show an apparent thickness-dependence and anisotropy. The relative uncertainty of in-plane thermal conductivity is ~20% for the thinnest film and reduced to <5% for thicker flakes. Results from the first-principles predictions assuming diffuse boundary scattering are also shown in Figure 2.13(c, d) as a comparison and will be discussed later.



Figure 2.13 Measurement of 2D-Te in-plane thermal conductivity using micro-Raman thermometry method. (a) Raman shift of A1 mode as a function of temperature with laser polarization along the chain and across the chain. The lines represent linear fitting. Inset: Four sample Raman spectra taken at varies bath temperatures. (b) Raman shift of A1 mode, representing Raman temperature rise, as a function of incident laser power. The lines represent the linear fitting. (c) Extracted in-plane thermal conductivities (κ//, κ<sub>+</sub>) of multiple 2D-Te films. Dashed lines are from first-principles calculations assuming no defects. (d) Extracted in-plane anisotropic thermal conductivity compared with first-principles prediction assuming a 0.1% defect level.

To measure the cross-plane thermal conductivity, tellurium flakes of varied thicknesses from the same batch for the in-plane thermal conductivity measurements are used. 2D-Te films with thicknesses about 50 – 200 nm are transferred to an ultra-clean silicon wafer and then coated with 70 nm of aluminum by electron-beam evaporation. Not enough sensitivity can be obtained for the films less than 50 nm. The cross-plane thermal conductivity is measured using the femtosecond time-domain thermo-reflectance (TDTR) technique(Cahill, 2004; Kang et al., 2008; Schmidt, Chen, & Chen, 2008; Zhao et al., 2016). The TDTR measured was performed by Mauricio Segovia, with the help from Dr. Yee Rui Koh. The TDTR measurement was conducted

using a Ti:Sapphire femtosecond laser wavelength centered at 800-nm with a 100-fs duration pulse laser at a repetition rate of ~80 MHz. The train of laser pulses is split into a pump beam and a probe beam using a beam splitter. Each beam is then linearly polarized with different orientations. The pump beam is then modulated at a frequency of 824 kHz, and passed through a delay stage creating a controlled delay between pump and probe pulses. The modulated pump beam and nonmodulated probe beam are then brought in focus to the surface of the coated sample. The radii of the focused pump and probe laser beams are ~6  $\mu$ m and ~5.5  $\mu$ m respectively. A ~70 nm thick aluminum film is deposited on the 2D-Te as an optical absorption layer and thermal reflectance transducer. The reflected light is filtered through a polarizer to allow only the probe light through, and the probe light is detected by a Si-photodetector. An RF lock-in amplifier is used to lock into the frequency of the modulated pump. Both the in-phase and out-of-phase signals (indicating the temporal change at the Al surface) are used to extract the cross-plane thermal conductivity by fitting to a 2-D transient heat diffusion model. A 2-D transient heat diffusion equation is used to fit the temporal temperature change at the surface to extract the thermal conductivity of the sample.

Figure 2.14(a) presents a typical (a 165-nm 2D-Te film) TDTR measurement data, the ratio of in-phase/out-of-phase signal vs. the delay time, fitted by the heat transfer model. The measured cross-plane thermal conductivities of films with various thicknesses are shown in Figure 2.14(b), together with the first-principles calculations which will be discussed below. The uncertainty of the fitting is about  $\pm 0.1$  W/m·K for thicker films and is about  $\pm 0.3$  W/m·K for thinner films.

The anisotropic thermal conductivities are summarized in Figure 2.13(c, d). We attribute the thermal conductivity largely to the lattice contribution because the electronic thermal conductivity is estimated to be ~0.1 W/m·K using electrical conductivity (Qiu et al., 2019) and Wiedemann-Franz Law assuming the Lorenz number between the single-band/nondegenerate and metal/highly-degenerated limits. The thermal conductivity along the chain of the stiff covalent bond  $\kappa_{l'}$  is 50-150% higher than that in the vdW bonded across-chain direction  $\kappa_+$  and  $\kappa_{\perp}$ . The anisotropic phonon dispersion in the along-chain ( $\Gamma$ -A or [0001]) direction and the across-chain direction originates from the contrasting bonding condition and is the main reason of this anisotropy of thermal conductivity. In addition, phonon transport in the cross-chain direction (both in-plane and out-of-plane) is suppressed more from surface scattering, as discussed further below.  $\kappa_{l'}$  is ~2.5 W/m·K for the near-bulk 100-nm thick film and reduces to ~1.6 W/m·K as film thickness decreases to 15 nm. Similar thickness dependence also observed  $\kappa_+$  and  $\kappa_+$ , decreasing from ~1.7

and 1.2 W/m·K to 0.6 and 0.8 W/m·K, respectively. This size-effect indicates strong surface scattering of long-MFP phonons. The surface scattering also affects electronic transport that reduced mobility, which is observed for thinner 2D-Te films (Wang et al., 2018). In a similar material Bi<sub>2</sub>Te<sub>3</sub> thin films, strong size effects of electronic and thermal transport due to surface scattering were also observed (Pettes et al., 2013). Compared with the experimental result of bulk thermal conductivity of  $\kappa_{l/l} = 3.38$  W/m·K,  $\kappa_{+} = 1.97$  W/m·K (Ho et al., 1972) and first-principles calculated values of  $\kappa_{l/l} = 2.77$  W/m·K,  $\kappa_{+} = 1.22$  W/m·K at room temperature (Peng et al., 2015), the values of the measured thermal conductivity of all samples are lower.



Figure 2.14 Measurement of cross-plane thermal conductivity using TDTR method. (a) Typical thermal reflectance trace in the time domain, curve fitted with best-fit thermal conductivity and its upper and low bounds. (b) Extracted cross-plane thermal conductivity of 2D-Te films at varies thicknesses, with first-principles predictions with (0.1% defects) and without defects.

First-principles calculations are carried out to help to understand the measured thermal transport properties. The calculation is performed by Dr. Xiaolong Yang and Prof. Xiulin Ruan. Figure 2.15(a) shows the calculated optimized structure of trigonal tellurium, which has a monoclinic phase with space group  $P_{3121}$ , and consists of helical chains arranged in a hexagonal array along the c-axis as seen earlier in Figure 2.11(a), while the a-axis is in the in-plane, cross-chain direction and the b-axis in the cross-plane (both perpendicular to the helical chains). Specifically, the intrachain and interchain distances are found to be 2.89 and 3.50 Å. The phonon dispersion and group velocities are shown in Figure 2.15(b, c), respectively. As is seen in Figure 2.15(c), group velocities along the chain direction are much larger than the other two directions, especially for phonons with a frequency below 2 THz. The relaxation time of the modes

contributing to the  $\kappa_{l'}$  and  $\kappa_{+}$  are presented in Figure 2.15(d), demonstrating a small difference in different directions. Thus, we conclude that the thermal conductivity anisotropy in the bulk is chiefly attributed to the anisotropic group velocity. We also show the calculated cumulative thermal conductivity of bulk Te at room temperature in Figure 2.15(e), with the bulk values of  $\kappa_{l'}$  and  $\kappa_{+}$  approaching 3.45 and 1.63 W/m·K, respectively (the sudden jump around  $\lambda$ =4000 µm should be artifact), agree better with the measurement result of bulk ( $\kappa_{l'}$  = 3.38 W/m·K,  $\kappa_{+}$  = 1.97 W/m·K) (Ho et al., 1972) than the previous prediction (Peng et al., 2015). It can also be seen that thermal conductivities of Te are mainly dominated by phonons with MFP below 100 nm (corresponds to 2 THz). This is the reason that the thermal conductivities of Te film are greatly affected by boundary scattering when the film thickness is below 100 nm.

The anisotropic thermal conductivities of 2D-Te films at room temperature are calculated considering the mode-wise effects from diffuse surface scattering (Figure 2.13(c) and Figure 2.14(b)). The measured data overall follows the trend of the predicted classical size effect, while the generally lower values from experiments are attributed to defects. Figure 2.15(f) shows the relative thermal conductivity as a function of the thickness of 2D-Te films. It can be observed that the cross-plane  $\kappa$  is reduced more than the other two directions due to additional scattering at the surface. For in-plane transport,  $\kappa_{l'}$  and  $\kappa_{+}$  are reduced to 80% of the bulk value for the 100 nmthick film, while the cross-plane  $\kappa_{\perp}$  is reduced to 70%. As the thickness decreases to 10 nm, we find that the  $\kappa_{\prime\prime}$ ,  $\kappa_{+}$ , and  $\kappa_{\perp}$  values sharply decrease to about 53%, 50%, and 32%, respectively. In the cross-plane direction, although it is also cross-chain, the thermal conductivity is reduced more than that of the in-plane cross-chain direction. This is because the boundary is perpendicular to the cross-plane  $\kappa_{\perp}$  direction, hence shortens the mean free path of the corresponding phonons more. In Ref (Majumdar, 1993), a similar scenario of dielectric thin films was observed. The effects of boundary scattering for reducing the thermal transport in different directions can be further characterized using the suppression function (Carrete et al., 2017; Dongre et al., 2018; Majumdar, 1993).



Figure 2.15 Modeling results of 2D-Te based on first-principles calculation. (a) Lattice structure and first-Brillion zone of trigonal tellurium. (b) Phonon dispersion of bulk trigonal tellurium on high-symmetry axes. (c) Phonon group velocities of the three directions as a function of frequency ω. (d) Relaxation time of phonon modes along different directions. (e) Cumulative thermal conductivity of bulk Te as a function of phonon MFP. (f) Relative thermal conductivities with increasing thickness of Te film.

The measured data in the three directions are generally lower than the calculation values and show some fluctuations with the thickness as mentioned above. We attribute these to the defects in 2D-Te films which is may not be homogeneous for different samples. Comparing with the first-principles calculation that accounts for the point defects, we found that the reduction of thermal conductivity can be roughly fit at a defect level of about 0.1% (Figure 2.13(d)), which is reasonable for liquid-phase synthesized thin films ( Lin et al., 2016) We also notice that recent proposals of covalent-like quasi-bonding, an inter-chain interaction with wavefunction hybridization stronger than the vdW force(Qiao et al., 2018; Xiang et al., 2019), which rises especially when Te or Se approaching 2D thin-film, may explain the smaller difference of  $\kappa_{//}$  and  $\kappa_+$  than the first-principles prediction.

To conclude Section 2.3, we measured the anisotropic thermal conductivities of 2D-Te in the in-plane along/across chain directions, as well as the cross-plane direction using micro-Raman thermometry and TDTR and studied the phonon transport processes using the first principles simulation. The thermal conductivities are intrinsically anisotropic and reduced by as much as 60% as the thickness decreases from 200 nm to 15 nm due to surface scattering of phonons, especially long-MFP phonons, while the anisotropy arises in both in-plane and cross-plane directions. Theoretical modeling of phonon dynamics illustrated that the anisotropy is chiefly attributed to the anisotropy phonon dispersion which stems from the contrast of covalent bond versus vdW interaction. The results reported here indicate the prospective of 2D-Te based high-performance thermoelectric generator/cooler at room temperature, also will support essential parameters for designing thermal systems for 2D-Te transistors and other electronic devices.

#### 2.4 Reliability of Raman measurements of thermal conductivity

Despite the abundant instances of 2D materials thermal transport studied using micro-Raman thermometry, there are still a few questions and even suspicion on the reliability of micro-Raman thermometry. Two of most challenging doubts on Raman method reliabilities that could have undermined the results in this section are: Local non-equilibrium phonons possibly exist due to the weak electron-phonon and phonon-phonon coupling, in which case the temperature of the exact phonon mode selected as Raman temperature transducer may not represent the real temperature rise.(Sullivan et al., 2017; Vallabhaneni et al., 2016) The other issue, the thermal strain during temperature calibration (uniformly heated) and during thermal conductivity measurement (locally heated at the center) are different. The Raman temperature transducer, despite in-situ calibrated, may not reliably work for the thermal conductivity measurement.

#### 2.4.1 Existence of Local Non-Equilibrium Phonons Affecting Raman Thermometry

The thermal energy dissipation process among different carriers is illustrated in Figure 2.16(a), with simplification to three (four for ones with flexural modes e.g., graphene) types of energy carriers. The photon energy of the visible light used in Raman thermometry is above the bandgap of most of the studied solids. Optical heating is hence mainly the energy exchange from photons to electrons. The hot electrons (in indigo) then transfer the thermal energy to different phonon modes and the rate depends on the intensities of electron-phonon coupling with each mode. The phonon modes also interact with each other towards thermal equilibrium. The acoustic phonons (LA, TA) (and flexural phonons ZA, ZO, e.g., in graphene, in cyan) contribute to most of the lattice thermal conduction. The optical phonons (LO, TO, in purple) contribute a smaller percentage, but the temperature determines the Raman signal. Hence there is a possibility that the temperature measured by Raman thermometry does not represent the optically heated local temperature rise.

In most scenarios, Raman thermometry is conducted using a continuous-wave laser (steady-state) and is not a concern since the relaxation times of e-ph and ph-ph are usually ~1 ps or lower so that all the carriers are near/in equilibrium. However, graphene is a very special case. The electron-phonon (e-ph) and/or phonon-phonon (ph-ph) coupling weak, esp. the prevented energy exchange between the flexural phonons and the 2D electrons with zero out-of-plane momentum due to the mirror symmetry w.r.t. the plane (Vallabhaneni et al., 2016), enabled the local generation of non-equilibrium carriers upon the laser heating. Besides that, the large mean-free-path (on the order of a few micrometers) for both electrons and phonons (due to both the weak coupling i.e. the long relaxation time, and the large group velocity) maintain the non-equilibrium of carriers for a large range of the suspension region (Sullivan et al., 2017) as shown in Figure 2.16(b). As a result, the optical phonon temperature measured by the Raman thermometry is insufficient to describe the temperature rise upon the laser heating, and a heat conduction model with multiple temperatures and thermal conductivities would be needed to obtain accurate results.



Figure 2.16 Temperatures of energy carriers during thermal conductivity measurements using the Raman method. (a) Energy dissipation processes. (b) Non-equilibrium temperature distribution in graphene (Gr) and other 2D thin films with stronger electron-phonon/phonon-phonon coupling and not-as-high mean-free-path.

On the other hand, the accuracy of thermal conductivity measured by the Raman method in our work is not much affected by the non-equilibrium. The phonon MFP in Bi<sub>2</sub>Te<sub>2</sub>Se and 2D-Te are below tens of nanometers as discussed in Section 2.2 and 2.3, much smaller than the laser spot size ~1  $\mu$ m. The carriers hence reach equilibrium after traveling a small distance after generated, and the temperature distribution is well-established between the optical heat source and the heat sink as illustrated in Figure 2.16(b). The conventional heat conduction model with a single unified temperature is valid and the thermal conductivity can be extracted as long as the temperature rise can be correctly measured. The generation rate (within the a with MFP as its radius) during the Raman measurement is estimated to be ~ 10<sup>11</sup> – 10<sup>12</sup> s<sup>-1</sup> (under the ~100  $\mu$ W 633-nm laser focused to a ~1  $\mu$ m spot). Comparing with the energy relaxation time of electrons (Iyer et al., 2019; Iyer, Chen, & Xu, 2018) ~10 ps for electrons and phonon relaxation times <1 ps (Section 2.2, 2.3), tens of carrier at most are excited before others relax or leave the sphere defined by the MFP. Hence the carriers are near-equilibrium even within the laser spot and the temperature measured by Raman thermometry. Now we can safely conclude that the local non-equilibrium of energy carriers in Bi<sub>2</sub>Te<sub>2</sub>Se and 2D-Te, and also other materials with smaller carrier MFP and lifetime, is negligible and does not affect the accuracy of the thermal conductivity measurement.

#### 2.4.2 Thermal Expansion Effects in Raman Measurements

In micro-Raman thermometry we used and many other cited practices above, the temperature-dependent Raman peak shift, i.e., the shift of the lattice vibrational frequency, is used as the temperature transducer. Due to the anharmonicity of the interatomic potential, the frequency shift responds to both temperature and strain in two ways (Lucazeau, 2003): The elongated atomic bonds are softened, resulting in a redshift of Raman peak responding to either mechanical stress or thermal expansion. Also, phonon-phonon interactions also contribute to the frequency shift (a pure temperature contribution, sometimes called the explicit contribution (Lucazeau, 2003)), namely, the interatomic potential can be tailored by lattice vibrational energy changes, arising from the altered phonon population per Bose-Einstein distribution at varying temperatures. This combined effect has been applied to map the temperature and strain distribution in, e.g., power electronic or piezoelectric devices directly and simultaneously (Bagnall et al., 2017; Beechem et al., 2008; Beechem et al., 2007). On the other hand, this temperature and strain complexity leads to concerns on the accuracy of the Raman-temperature transducer, and this uncertainty propagates into the thermal conductivity per the procedure we presented in the above sections. Here, it is important to understand that the temperature coefficient may vary for the sample at different mechanical states, i.e., when the sample is suspended or supported on a substrate. Furthermore, even if the temperature calibration and the thermal conductivity measurement are performed with the laser focused at the same spot of the suspended region (Figure 2.17), there is still a question if this "suspended Raman temperature coefficient" obtained when the entire sample is uniformly heated in the thermal bath during calibration, can be used when locally heated during the thermal conductivity measurement, since the strain distribution in these two cases can be different. A series of thermal and mechanical calibration method was first proposed to resolve this issue for our work in Section 2.2 reported in the Supplementary Note of Ref. (Luo et al., 2018). Here, we further improved the series of calibration procedure and performed a comprehensive study taking an wellstudied material, exfoliated thin-film Bi<sub>2</sub>Te<sub>3</sub> (Goldsmid, 1956; Heremans, Cava, & Samarth, 2017; Pettes et al., 2013; Taylor, 1961; Teweldebrhan et al., 2010; Wang et al., 2013; Wang et al., 2013), as an example to evaluate the temperature and strain effects in micro-Raman thermometry.



Figure 2.17 Schematic of laser focusing at the center of the suspended thin film sample, locally heating inducing Raman scattering as temperature transducer, also resulting in local thermal expansion.

Similar to Section 2.2, Bi<sub>2</sub>Te<sub>3</sub> thin films are tape-exfoliated from the bulk crystals grown using the Bridgman method (Bridgman, 1925). For thermal conductivity measurement, the thin film is suspended on holey SiN membranes using the PVA/PMMA wet transfer technique (Bertolazzi, Brivio, & Kis, 2011; Bonaccorso et al., 2012; Dean et al., 2010; Luo et al., 2015, 2018). Raman thermal conductivity measurements (Raman shift vs. incident power) are also similarly performed.

Now we address the validity of the Raman-temperature calibration for the mechanical condition of suspended film. We consider a general case of Raman shift with coexisting temperature rise and mechanical strain. In the following discussion on Raman coefficients, we use  $\varsigma$  for the material properties in theory, and  $\chi$  for the experimental measurables. The total Raman shift  $\Delta \omega$  can be written as in Eq. 2.9, considering both strain and phonon-phonon scattering contribute to the total Raman shift.  $\varsigma_{T}$  is the pure temperature coefficient or the Raman-temperature coefficient with lattice constants fixed with respect to the value at room temperature, referred to as "strain free", and  $\varsigma_{e}$  is the Raman-strain coefficient for uniaxial strain; and  $\alpha$  is the thermal expansion coefficient.  $\sigma_{i}$  is the mechanical stress applied in the *i*-axis, and *E* is Young's modulus, and v is the Poisson ratio. The first term on the right-hand side is the Raman shift of pure temperature contribution (only due to the phonon-phonon interactions). The parentheses summarize the total (hydrodynamic) strain. The first term in the parentheses is the Raman shift due to thermal expansion, and the second term is the response to the normal mechanical strains.

Depending on the mechanical boundary condition, different strain/stress can be induced in the sample, which can cause different Raman shift vs. temperature rise. The last term on the righthand side represents the higher-order and covariant terms, which are expected to be negligible for small perturbations. We will also empirically show that it is indeed negligible.

$$\Delta \omega = \varsigma_T \Delta T + \varsigma_{\varepsilon} \sum_i \left( \alpha_i \Delta T + \sigma_i \frac{(1-\nu)}{E} \right) + o(T,\varepsilon)$$
(2.9)

The thermal expansion coefficient of SiN  $(3.3 \times 10^{-6} \text{ K}^{-1})$  is smaller than that of most of the thin-film materials (including bulk Bi<sub>2</sub>Te<sub>3</sub> ~  $1.5 \times 10^{-5} \text{ K}^{-1}$  (Pavlova, Shtern, & Mironov, 2011; Taylor, 1961)), thus the suspended films experience compression during both the uniform heating (calibration) and local heating cases. It is likely that the mechanical stress in suspended nanometer-thin films to be released due to buckling due to the large aspect ratio of thickness (tens of nm) and lateral size (several µm). The critical buckling strain of circular suspended films can be estimated using the Euler's stability formula of drum surfaces (a suspended film (~0.2 for Bi<sub>2</sub>Te<sub>3</sub>), *t* is the thickness, and *R* is the radius of the circular suspension region. Taking the Bi<sub>2</sub>Te<sub>3</sub> thin films reported in this work (6-30 nm) as an example, the critical buckling strain is estimated to be ~2×10<sup>-6</sup> - 5×10<sup>-5</sup>, corresponding to the thermal expansion from a temperature rise of 0.15-4 K. Hence the suspended thin film samples achieve stress-free during the optothermal Raman tests with a typical temperature rise of tens of Kelvins in the experiments.

$$\varepsilon_{\rm c} = \frac{2.16^2}{12(1-\nu^2)} \left(\frac{t}{R}\right)^2 \tag{2.10}$$

In this suspension and buckling scenario, Eq. 2.9 can be simplified to Eq. 2.11, describing the free thermal expansion. It is worth noticing that this reorganizing of terms introduces another Raman-temperature coefficient at the stress-free condition  $\chi_{T,\sigma=0}$  shown in Eq. 2.11 which is defined by the material properties  $\varsigma_T$ ,  $\varsigma_{\varepsilon}$ , and  $\alpha$ . The definition of  $\chi_{T,\sigma=0}$  is hence not specified to the detailed strain distribution, but is applicable as long as the film is stress-free. The Ramantemperature coefficient calibrated at the center of the suspension region  $\chi_T$  is in essence the stressfree Raman temperature coefficient defined here.

$$\Delta \omega = (\varsigma_T + 2\varsigma_{\varepsilon}\alpha)\Delta T = \chi_{T,\sigma=0}\Delta T \tag{2.11}$$

Next, we confirm the linearity and decoupling of the Raman coefficients before the suspended  $\chi_T$  can be confidently used in the thermal conductivity measurement. We present below

a systematic series of calibrations to show that the Raman responses of temperature and strain are linear and the  $o(T, \varepsilon)$  terms in Eq. 2.9 are negligible within the range during the thermal conductivity measurement. This series of studies consists of temperature calibration of thin-film samples supported on three different types of substrates, and a calibration using a mechanical bending test at room temperature.

Thin films are transferred onto fused silica, silicon, and sapphire substrates to perform the Raman-temperature calibration. The PDMS stamping method was used to peel and transfer the films from one substrate to another to maximize the consistency of the sample used. For each case, a few samples ranging from 10 - 30 nm are examined to account for the uncertainties due to sample-to-sample variation. The Raman thermometry is conducted for the samples immerged in a nitrogen environment and a thermal bath of temperature ranging from room temperature to ~100°C, and one typical set of results are summarized in Figure 2.18. Figure 2.18(a) showed the peak shift of the  $E_g^2$  mode of which is selected to be the temperature coefficient. The Raman shift vs. bath temperature of the thin film supported on fused silica, silicon, and sapphire substrates are plotted and linear fitted in Figure 2.18(b, c, d) respectively. The Raman-temperature coefficients increase with the thermal expansion coefficients of the substrates. The thermal expansion coefficients (provided by the vendors) and the corresponding Raman-temperature coefficients are summarized in Table 1.

	α (×10 <sup>-6</sup> K <sup>-1</sup> )	$\chi_{T,s} (cm^{-1}/K)$	
Fused silica	0.55	-0.0110	
Silicon (100)	2.6	-0.0136	
Sapphire (0001)	6.95	-0.0170	

Table 2.2 Thermal expansion coefficients and Raman-temperature coefficients of Bi<sub>2</sub>Te<sub>3</sub> thin film supported on substrates



Figure 2.18 Raman thermometry: temperature calibration of  $Bi_2Te_3$  thin film supported on varied substrates (a) Raman spectra of  $Bi_2Te_3$  thin film under different temperature supported on fused silica. (b, c, d) Raman shift of  $E_g^2$  mode vs. bath temperature on (b) fused silica (c) silicon and (d) sapphire.

Raman measurements when  $Bi_2Te_3$  thin films supported on Si substrates are subject to mechanical uniaxial bending are performed using a home-made bending tool, as shown in **Error! Reference source not found.**(a) The strain is controlled using a pair of micrometers. The tensile strain on the top surface of the Si wafer ( $t = 525 \mu m$ ) can be calculated using the beam equation Eq. 2.12 (Lund & Finstad, 2004), where  $d_z$  is the deflection plate in the vertical direction, t is the wafer thickness, and a and L are the dimensions (nearest and farthest points) of the contact points of the bending tool. The Raman spectra of the  $Bi_2Te_3$  thin film at given calculated tensile strain are shown in **Error! Reference source not found.**(b). We again select the  $E_g^2$  mode of  $Bi_2Te_3$  as its Raman strain transducer, and the  $E_g^2$  mode Raman shift are fitted and plotted against the applied mechanical strain calculated from the micrometer readings as shown in **Error! Reference source not found.**(c). The linearity of Raman shift vs. strain relation, as shown in **Error! Reference**
**source not found.**(c), leads to a constant Grüneisen parameter  $\gamma$  (Eq. 2.13,  $\varsigma_{\varepsilon} = \gamma \omega_0$ ) which is a signature of the no-slip condition during the mechanical bending tests (Wu et al., 2018). According to Eq. 2.9, the Raman strain coefficient obtained from the uniaxial bending test is  $\chi_{\varepsilon} = (1 - \nu_{Si})\varsigma_{\varepsilon}$ . Using the Poisson ratio of silicon ( $\nu_{Si} = 0.25$ ) and the averaged slope in the uniaxial bending tests, the Raman-strain coefficient  $\varsigma_{\varepsilon}$  is extracted to be -4.324 cm<sup>-1</sup>/%. It is also confirmed that the no-slip interface condition by strain cycling that the Raman shift followed the same line as the tensile strain is released.



Figure 2.19 Raman response to uniaxial strain (a) Four-point bended thin film samples measured by Raman spectroscopy. (b) Raman spectra of  $Bi_2Te_3$  thin film under different temperatures supported on Si substrate. (c) Raman shift of  $E_g^2$  mode of  $Bi_2Te_3$  thin film vs. mechanical uniaxial strain. Inset: atomic force microscope image of the  $Bi_2Te_3$  thin film. (d) The strain calculated from the micrometer and the strain extracted from Raman shift of silicon of the data points. inset:  $E_g^2$  mode Raman shift of the  $Bi_2Te_3$  thin film vs. the corresponding Raman shift of silicon.

We would also want to point out that there is no slip at the heterointerface of supported samples and the substrates during the temperature calibrations because the maximum strain applied in the bending test is greater than the differences of thermal expansion between sample and substrate. Furthermore, the Raman response of silicon is examined to verify the correctness of the applied strain. In **Error! Reference source not found.**(d), the uniaxial strains of the Si top surface calculated using Eq. 2.13 and the micrometer readings are compared with those extracted from the Raman shift. The strains obtained from the two methods can be linearly fitted with a < 7% discrepancy between their slopes. The Raman responses of Bi<sub>2</sub>Te<sub>3</sub> and Si are also plotted in **Error! Reference source not found.**(d) and fall on one line. We hence validate that the strain is correctly applied to thin-film samples.

$$\varepsilon = \frac{3d_z t}{a(3L - 4a)} \tag{2.12}$$

$$\gamma = -\frac{V}{\omega_0} \frac{\partial \omega_0}{\partial V} = -\frac{\Delta \omega_0}{\varepsilon_n \omega_0} = -\frac{\Delta \omega_0}{\varepsilon_{\parallel} (1 - \nu_{\rm Si}) \omega_0}$$
(2.13)

Now we summarize the calibration data described above to show that the Raman responses to temperature and strain can be expressed as a linear combination, and the higher-order and covariance terms can be safely neglected during the thermal conductivity measurement. During the temperature rise in the thermal bath, the thin film samples experience isotropic strain according to the thermal expansion of the substrates. The Raman shift of the supported thin film on a certain substrate (subscript "s") and the corresponding temperature coefficient  $\chi_{T,s}$  can thus be written as Eq. 2.14(a, b), which is a generalization of Eq. 2.11. Performing the temperature calibration of the thin films on substrates with different thermal expansion coefficients provides additional data points and improves the fidelity of the strain-temperature decoupling. In Figure 2.20, we summarize the Raman-temperature coefficient obtained from samples supported on fused silica, silicon, and sapphire. The error bars represent the uncertainties due to sample-to-sample variation when multiple samples (ranging from 10 - 30 nm) used. The fitted slope is very close to the Raman-(hydro)strain coefficient  $2\varsigma_{\varepsilon}$  (the factor of 2 comes from biaxial thermal expansion) as we suggested in Eq. 2.11. Here we plot the (red dashed) fitting line with the slope prescribed as  $2\varsigma_{\varepsilon}$ , and the temperature calibration results fall on this fitting line within the uncertainties. The temperature and strain calibration results in Figure 2.20 hence show high fidelity of the superposition of the temperature and the strain effects, and the negligible higher-order/covariance terms within the experimental uncertainty. The result of calibration of a suspended film (Figure 2.20 inset) is also included in Figure 2.20 as the green triangle. The fact that the green triangle falls on the line indicates that expansion of the film is determined by the its own thermal expansion, hence it is buckled to release stress.(Zhang et al., 2019) It is found that both thermal expansion determined by the substrate and intrinsic phonon-phonon interactions of the film contribute a significant percentage to the temperature-dependent Raman shift. The Raman temperature coefficients obtained from different substrates can vary by more than 50% from -0.011 cm<sup>-1</sup>/K to -0.017 cm<sup>-1</sup>/K, depending on thermal expansion of the substrate. On the other hand, the temperature calibration at the buckled suspended region associates neither with external material properties nor the local strain distribution. Hence in the thermal conductivity measurement, it is critical to use the temperature coefficient calibrated for the suspension film as the thermal transducer.

$$\Delta\omega = \left(\varsigma_{\mathrm{T},\varepsilon=0} + 2\alpha_{\mathrm{s}}\varsigma_{\varepsilon}\right)\Delta T \tag{2.14a}$$

$$\chi_{\mathrm{T,s}} = \varsigma_{\mathrm{T}} + 2\alpha_{\mathrm{s}}\varsigma_{\varepsilon} = \varsigma_{\mathrm{T}} + \frac{2\alpha_{\mathrm{s}}\chi_{\varepsilon}}{1 - \nu_{Si}}$$
(2.14b)



Figure 2.20 Summary of the Raman-temperature coefficient calibrated on substrates with different thermal expansion coefficients (blue circles) and fitted by the slope of Raman-(hydro) strain coefficient of  $2\varsigma_{\varepsilon}$ = -8.648cm<sup>-1</sup>%<sup>-1</sup>. Inset: Raman shift of E<sub>2g</sub> mode vs. bath temperature of

# suspended Bi<sub>2</sub>Te<sub>3</sub> thin film (temperature coefficient included in the main figure as the green triangle).

Furthermore, we want to point out and resolve the issue that method above failed to treat the exact dependence of a specific phonon mode on the triaxial strain condition. The response of the phonon mode can be obtained from the character table of its group representation as introduced in Section 2.1. The character group for  $Bi_2Te_2Se$  is given as Table 2.3.(Dresselhaus et al., 2008)

$D_{3d} = D_3 \otimes i(\bar{3}m)$			E	$2C_{3}$	3 <i>C</i> <sub>2</sub> '	i	$2iC_3$	$2iC_2$ '
$x^2 + y^2, z^2$		$A_{1g}$	1	1	1	1	1	1
	Rz	$A_{2g}$	1	1	-1	1	1	-1
$(xz, yz), (x^2 - y^2, xy)$	$(R_x, R_y)$	$E_{ m g}$	2	-1	0	2	-1	0
		$A_{1u}$	1	1	1	-1	-1	-1
	z.	$A_{2u}$	1	1	-1	-1	-1	1
	(x, y)	$E_u$	2	-1	0	-2	1	0

Table 2.3 Character table for group  $D_{3d}$  (rhombohedral)

Among the terms in the deformation potential of the lattice, Vxx + Vyy and Vzz belong to  $A_{1g}$  mode and Vxy, Vyz, and Vxx - Vyy, Vxy belong to  $E_g$  mode. Thus, the deformation potential can be represented by  $\Gamma_V = A_{1g} + E_g$  and the deformation potential can be reorganized to the quadratic form per the basis  $A_{1g}$  and  $E_g$ . The phonon frequency of the Raman active mode M can be determined by the deformation matrix element. Due to the large aspect ratio, the shear deformation of  $\varepsilon_{xz}$  and  $\varepsilon_{yz}$  can be neglected.

$$V = \sum_{ij} V_{ij} \varepsilon_{ij} = \frac{1}{2} (V_{xx} + V_{yy}) (\varepsilon_{xx} + \varepsilon_{xx}) + V_{zz} \varepsilon_{zz} + 2 (V_{xz} \varepsilon_{xz} + V_{yz} \varepsilon_{yz}) + \frac{1}{2} [(V_{xx} - V_{yy}) (\varepsilon_{xx} - \varepsilon_{yy}) + 4 V_{xy} \varepsilon_{xy}] \Delta \omega_{M} = \frac{1}{\hbar} \langle M | V | M \rangle$$
(2.15b)

Using the character table Table 2.3, the direct product  $A_{1g} \otimes E_g = E_g$ , does not contain  $A_{1g}$ , i.e. the corresponding matrix element  $\langle A_{1g} | V_{ij} | A_{1g} \rangle$   $(i \neq j)$ ,  $\langle A_{1g} | V_{xx} - V_{yy} | A_{1g} \rangle$  are null. The phonon frequency shift of  $A_{1g}$  mode is given by

$$\Delta\omega_{A_{1g}} = \chi^{(1)}_{\varepsilon,A_{1g}} \left( \varepsilon_{xx} + \varepsilon_{yy} \right) + \chi^{(2)}_{\varepsilon,A_{1g}} \varepsilon_{zz}$$
(2.16)

where  $\chi_{\varepsilon,A_{1g}}^{(1)} = \frac{1}{2\hbar} \langle A_{1g} | V_{xx} + V_{yy} | A_{1g} \rangle$ , and  $\chi_{\varepsilon,A_{1g}}^{(2)} = \frac{1}{\hbar} \langle A_{1g} | V_{zz} | A_{1g} \rangle$  are the strain coefficient deduced from the deformation matrix elements  $A_{1g}$  for mode.

The  $E_g$  mode is two-fold degenerated as introduced in Section 2.1 and the phonon frequency shift is obtained by solving the Eigen equation of deformation.

$$\begin{vmatrix} \chi_{\varepsilon,E_{g}}^{(1)}(\varepsilon_{xx}+\varepsilon_{yy})+\chi_{\varepsilon,E_{g}}^{(2)}\varepsilon_{zz}+\chi_{\varepsilon,E_{g}}^{(3)}(\varepsilon_{xx}-\varepsilon_{yy})-\Delta\omega_{E_{g}} & 2\chi_{\varepsilon,E_{g}}^{(4)}\varepsilon_{xy} \\ 2\chi_{\varepsilon,E_{g}}^{(4)}\varepsilon_{xy} & \chi_{\varepsilon,E_{g}}^{(1)}(\varepsilon_{xx}+\varepsilon_{yy})+\chi_{\varepsilon,E_{g}}^{(2)}\varepsilon_{zz}-\chi_{\varepsilon,E_{g}}^{(3)}(\varepsilon_{xx}-\varepsilon_{yy})-\Delta\omega_{E_{g}} \end{vmatrix} = 0 \quad (2.17a)$$

$$\Delta\omega_{E_{g}} = \chi^{(1)}_{\varepsilon, E_{g}} \left( \varepsilon_{xx} + \varepsilon_{yy} \right) + \chi^{(2)}_{\varepsilon, E_{g}} \varepsilon_{zz} \pm \sqrt{\chi^{(3)2}_{\varepsilon, E_{g}} \left( \varepsilon_{xx} - \varepsilon_{yy} \right)^{2} + 4\chi^{(4)2}_{\varepsilon, E_{g}} \varepsilon^{2}_{xy}}$$
(2.17b)

Now the complete information of phonon frequency shift responding to any complex strain condition is obtained in Eq. 2.16 and 2.17(b). Notice the shift of  $E_g$  mode decomposes into two frequencies, representing the phonons redshift under tensile strain parallel to the uniaxial stress direction and the blueshift under compressive strain in the transverse direction per the Poisson ratio. This peak splitting, though can be treated in the Grüneisen parameter framework for the cases under a uniaxial strain (Mohiuddin et al., 2009) as given in Eq. 2.18, is in fact a result of the removal of degeneracy of the mode deduced by the group representation. The generic strain-Raman relation can be similarly analyzed and derived, and applied for temperature/strain calibration under more complex conditions.

$$\Delta\omega_{E_{g}} = \Delta\omega_{E_{g},n} \pm \frac{1}{2} \Delta\omega_{E_{g},shear} = -\omega_{E_{g},0} \gamma_{E_{g}} (\varepsilon_{\parallel} + \varepsilon_{+} + \varepsilon_{\perp}) \pm \frac{1}{2} \frac{\partial\omega_{E_{g},shear}}{\partial\varepsilon_{shear}} (\varepsilon_{\parallel} - \varepsilon_{+}) \quad (2.18)$$

To conclude, we used a series of testing and calibration procedures to study the complex temperature vs. strain response during optothermal micro-Raman measurements of in-plane thermal conductivity of thin films. These studies showed the Raman response to temperature and thermomechanical strains are both linear and can are superimposed. The stress-free Raman temperature coefficient can be defined which is not specific to detailed strain distribution. The results justified the Raman temperature coefficient obtained at the center of a suspended thin film as a valid temperature transducer for thin films with tens of nanometer thickness that experience buckling. On the other hand, our studies showed that the calibration performed on supported samples would fail to serve this purpose due to the thermal expansion of the substrate. The relation between Raman shifts of certain modes and triaxial strain condition is also derived from group

theory perspective for more detailed analyses, and can also be adapted into the Grüneisen parameter framework for a more practical experimental procedure.

#### 2.5 Summary

This chapter mainly presented the thermal conductivity measurements for 2D thin films using micro-Raman thermometry. The thickness-dependent thermal/electrical conductivity measurement resulted showed a larger contribution of TSS to heat and charge transport, both exceeding 50% in sub-20-nm thin films. The extracted Lorenz number of TSS electrons was found more than 10 times larger than the ordinary electrons in solids, inferring an unconventional scattering mechanism of the TSS and its potential application in novel thermal devices. Anisotropic thermal conductivity was observed in 2D-Te. Incorporating with first-principles analysis, the anisotropic was identified to be originated mainly from the anisotropic group velocity of the lattice and the suppression from the surface of films. The concerns of reliability in the Raman method for thermal conductivity measurement were addressed. The decoupling of temperature and strain effects and detailed strain-dependent phonon frequency shifts make made toolkits for measuring thermal expansion coefficient measurements and analyzing complex strain conditions. The results in this chapter validated the Raman method as an effective tool for novel nanodevices developments.

## 3. HELICITY-CONTROLED TRANSPORT IN TOPOLOGICAL SURFACE STATES

In this chapter, the spin-polarized transport of the topological surface state is studied. The spin polarization of topological surface states is selectively excited using circularly polarized light. Linear polarization is converted to circular using waveplates or phase retarders for optical helicity incidence. The electrical current is a clear and easily accessible signal of the optical helicity-controlled transport process in TSS and serves as a reference for thermal transport. The electrical gate and bias voltages are used to maximize the TSS dominance, also used as knobs for parametric studies unveiling the transport characteristics. Optical polarization is first reviewed. The photocurrent measurements of TI devices are then presented in this chapter and the key findings are prepared in the contexts of photo-thermoelectricity tuning (Huang et al., 2020b) and optical chirality detection (Huang & Xu, 2021). This chapter is prepared with permission to reuse these contents. Copyright © 2020 Nature Publishing Group and 2021 John Wiley and Sons.

#### **3.1** Generating and Analyzing Optical Polarization States

Polarization of a light beam, i.e., the direction of the electric field vector, plays a critical role when interacting with matters. In general, a monochromatic plane wave from a single oscillator (coherent) is elliptically polarized per the profile that the E-field traces out as the wave propagates. The linear polarization makes a difference when it aligns differently with the plane of incidence as described using Fresnel equation for TE/TM mode, also depending on the alignment with optical axis/es in anisotropic (birefringent) materials. The circular polarization can be understood as photons with  $\pm\hbar$  angular momentum thus circular polarization-dependent optical properties are usually related to chiral (mirror-symmetry breaking) structures or spin/orbital angular momentum of electrons.

Jones vectors (Eq. 3.1) use the projections of the E-field vector, including the intensity and phase, on the two axes perpendicular to the propagation direction to represent the polarization state. Polarization optical elements, including polarizers (selectively pass or remove certain polarizations), phase retarders (introduce a certain phase difference to the polarizations, ones in transmission mode are called waveplates), rotators (rotate the polarization direction by a certain

angle), can be represented by Jones matrices acting on Jones vectors according to the net effects. The Jones matrices of these optical elements can be found in optics textbooks e.g., Ref. (Pedrotti, Pedrotti, & Pedrotti, 2017).

$$\vec{E}_{0} = \begin{bmatrix} E_{0x} e^{i\varphi_{x}} \\ E_{0y} e^{i\varphi_{y}} \end{bmatrix} = \frac{1}{\sqrt{A^{2} + B^{2} + C^{2}}} \begin{bmatrix} A \\ B + iC \end{bmatrix}$$
(3.1)

In most of the experiments presented in this chapter, a quarter waveplate (QWP, made of birefringent materials) is used to introduce a  $\pi/4$  phase delay and generate circular polarization. The output polarization with slow axis aligned at an angle  $\alpha$  from vertical linear polarization can be treated using Jones matrices as in Eq. 3.2. The Jones matrix of a QWP  $M_{QWP} = e^{-\frac{i\pi}{4}} \begin{bmatrix} 1 & 0\\ 0 & i \end{bmatrix}$  is applied onto the Jones vector of incoming linear polarization in vertical direction  $\begin{bmatrix} 0\\ 1 \end{bmatrix}$ . The rotation of the QWP is represented by the rotation operator  $\begin{bmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{bmatrix} M \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix}$ . (Notice the representations are normalized hence the equal signs are not necessarily mathematically equal). At  $\alpha = \pm \pi/4$ , the output polarization is left-hand or right-hand circular polarized (LCP or RCP).

$$\vec{E}_{out} = \begin{bmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{bmatrix} e^{-\frac{i\pi}{4}} \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \sin 2\alpha \\ \cos 2\alpha + i \end{bmatrix}$$
(3.2)

The other optical element used to generate circular polarization is the reflective phase retarder (RPR). RPRs are designed in the total internal reflection regime, and the phase difference is introduced differently for TE and TM wave as following Eq. 3.3, where  $\theta$  is the incident angle, and *n* is the ratio of refraction indices. Instead of rotating the RPR, which is not effective due to its isotropy, the input polarization is rotated to obtain circular polarization. When the polarization is  $\pm 45^{\circ}$  to the plane of incidence, the TE and TM components are equal and the output of the quarter-wave RPR is circular polarized. Fresnel rhombs are designed in the same principle with multiple total internal reflections in the optical crystal e.g., glass/CaF<sub>2</sub>. The weak dispersion allowed the elements to operate in a wider range of wavelengths.

$$\phi_{TE} = 2 \arctan\left(-\frac{\sqrt{\sin^2 \theta - n^2}}{\cos \theta}\right)$$
(3.3a)

$$\phi_{TM} = \pi - 2 \arctan\left(-\frac{\sqrt{\sin^2 \theta - n^2}}{n^2 \cos \theta}\right)$$
(3.3b)

The plane wave polarization state is characterized by a set of independent Stokes parameters, namely  $S_0 = E_x E_x^* + E_y E_y^*$  representing the total intensity,  $S_1 = E_x E_x^* - E_y E_y^*$  and

 $S_2 = E_x E_y^* + E_y E_x^*$  characterizing the linear polarization, and  $S_3 = i(E_x E_y^* - E_y E_x^*)$  quantifying the degree of circular polarization (McMaster, 1954). Here, all four parameters are required to represent the wave, including the intensity *I* (Eq. 3.4a), also the partially or unpolarized light wave originated from independent oscillators, e.g., thermal radiation. When the light is elliptically polarized (degree of polarization p = 1, Eq. 3.4b), the independent variables reduce to three: remaining the orientation of linear polarization ( $\psi$ , Eq. 3.4c) and the degree of circular polarization ( $p_c$ , Eq. 3.4d, i.e., the percentage of circular polarization intensity). Using Eq. 3.4d, one can obtain the output circularly polarized light in Eq. 3.2 with the rotating QWP  $\alpha$  is  $p_c = \sin 2\alpha$ , i.e., the circular output from the QWP has a  $\sin 2\alpha$  dependence. At QWP angle  $\alpha = 0$  and converted to right/left-hand circular polarized at  $\alpha = \pi/4$  and  $5\pi/4$ , and  $\alpha = 3\pi/4$  and  $7\pi/4$  respectively.

$$I = S_0 \tag{3.4a}$$

$$p = \sqrt{S_1^2 + S_2^2 + S_3^2/S_0} \tag{3.4b}$$

$$\tan(2\psi) = S_2/S_1 \tag{3.4c}$$

$$p_{\rm c} = S_3/S_0$$
 (3.4d)

A linear polarizer (LP) can be used as the analyzer to obtain three of the four Stokes parameters. The intensity measured after the LP at angle  $\beta$  from the *x*-axis is denoted as  $I_{\beta}$ . By definition, the three Stokes parameters can be determined as  $S_0 = E_x E_x^* + E_y E_y^* = I_{\beta_0} + I_{\beta_0 + \pi/2}$ ,  $S_1 = E_x E_x^* - E_y E_y^* = I_0 - I_{\pi/2}$ , and  $S_2 = E_x E_y^* + E_y E_x^* = I_{-\pi/4} - I_{\pi/4}$ . Besides, the axis and intensity of the linear polarization component can be obtained by rotating the linear polarizing analyzer over  $\pi$ . The circular component cannot be discerned from unpolarized using only an LP and a circular polarizer is not widely available. On the other hand, a QWP can be added to convert the circular polarization to linear, and then be analyzed by an LP.

The polarization analyses discussed above require multiple optical elements and rotating optomechanical components. This is due to the lack of intrinsic anisotropic or chiral response in common semiconductors such as silicon and III-V semiconductors from which photodetectors are made, thus, miniaturization of single-device or on-chip polarization analyzer is challenging. Some high-mobility semiconductor materials e.g., black phosphorus and tellurium with high anisotropy are candidates for linear polarization detection and the performance can be enhanced by optical nanostructures. (Tong et al., 2020; Venuthurumilli, Ye, & Xu, 2018) One direction of seeking chirality detecting devices is using intrinsically chiral materials including chiral dyes and liquid crystals. The first organic-semiconductor transistor for chirality detection utilized chiral helicene

(Yang, Da Costa, Fuchter, & Campbell, 2013) and hybrid perovskite devices were explored by combining the chiral-sensitive absorbing organic material and inorganic compound to enhance the optoelectronic performance. (Chen et al., 2019) The invention of metamaterials or metasurfaces, i.e., fabrication of sub-diffraction-limited nanostructures, enabled chiral optical properties beyond those offered by naturally existing materials. Metamaterials with helical nanostructures, for example, spirals that lack mirror symmetry, exhibit chirality-dependent absorption/transmission, and have been shown to achieve direct chirality detection. (Chen et al., 2010; Frank et al., 2013; Gansel et al., 2009; Li et al., 2015; Zhang et al., 2018; Zhu et al., 2018) Alternatively, metamaterials and metasurfaces also demonstrated the capability of manipulating polarization states, (Papakostas et al., 2003) and could function as ultracompact optical elements including linear/circular polarizers, (Gansel et al., 2009) waveplates/phase-retarders, (Yu et al., 2012) and polarizing beam splitters.(Turner et al., 2013) Fabricating these optical elements on top of conventional photodetectors can resolve the optical chirality(Zhao, Belkin, & Alù, 2012; Zhao et al., 2017) or extract the full Stokes parameters. (Basiri et al., 2019) In the next section, the helical photoresponse of TSS will be introduced, and the complete solution for polarization analysis is presented.

#### 3.2 Circular Photogalvanic Effect in Topological Surface States and More

The tetradymite family 3D TIs introduced in Chapter 1 are a new phase of quantum materials with TSS on the surface.(Hasan & Kane, 2010; Moore, 2010) The spin texture of the TSS electrons is locked to their momentum, so that the spin polarization can be induced by a current (electron motion with certain momenta), (Tian et al., 2019; Tian et al., 2017; Tian et al., 2015) and conversely, spin injection to the TSS can lead to a measurable current (McIver et al., 2011). The quantum picture is that photons of circularly polarized light with the spin angular momentum of  $\pm 1\hbar$  can interact with (flip) the electrons with spin  $\mp \frac{1}{2}$  during a selective excitation according to angular momentum conservation. The optical injection of spin polarization of TSS results in a circularly-polarized-light-controlled photocurrent which is phenomenologically called circular photogalvanic effect (CPGE). This helical photoresponse originated from TSS is first observed in Bi<sub>2</sub>Se<sub>3</sub> (McIver et al., 2011). Following up researches identified the origin of TSS by separating the photoresponse in the timescale using Auston-switch-based ultrafast photocurrent

measurement (Kastl et al., 2015); and by tuning the chemical potential and incident light wavelength (Duan et al., 2014; Okada et al., 2016; Pan et al., 2017). The intensity of the CPGE current is hence a figure of merit of the optical spin injection or angular momentum selective photo-generation of TSS.

The TI thin films were exfoliated using Nitto dicing tapes from Bi<sub>2</sub>Te<sub>2</sub>Se bulk crystals grown by Bridgeman method, then transferred onto 50-nm SiO<sub>2</sub>/Si substrate. A 0.7-nm Al layer was evaporated (then naturally oxidized into Al<sub>2</sub>O<sub>3</sub> when exposed to air) to protect the sample surface. The contact is patterned by e-beam lithography or photolithography, dipped in buffered oxide etcher to remove the  $Al_2O_3$ , and deposited by evaporation Cr/Au of 5/50 nm, for electrical measurement via Ni contact probe tips, or Cr/Au 5/95 nm for ones packaged by Au wire-bonding. The schematic measurement setup is shown in Figure 3.1(a). The 633-nm He-Ne laser beam was focused by an off-axis mirror (spot size ~5 µm) and incident to the sample at 45°. The nonrefractive optical setup allows another 1550-nm diode laser and a 10.6-µm to be also collimated and overlapped with / guided by the 633-nm laser for wavelength-dependent measurements. The laser beam is modulated by a mechanical chopper at 822 Hz. The photocurrent is first amplified/filtered by a current-preamplifier then measured by a lock-in amplifier at the chopping frequency. The bias voltage can be supplied by the current-preamplifier and the gate voltage (across the source contact and doped-Si gate) can be supplied by a DC source-meter grounded at the same potential as the amplifiers. Alternatively, the DC source-meter can also be directly used to measure the current and its two channels can serve as the bias and gate. In this case, the chopper can be removed since it's not a lock-in measurement. The 2D spatial mapping is realized by synchronizing the current measurement with a piezoelectric nano-positioner. All measurements are performed at room temperature.

Since the tetradymite TI  $Bi_2Te_2Se$  is also a good thermoelectric material, the laser heating induces the photo-thermoelectric (PTE) effect and leads to a clear pattern as shown in Figure 3.1(b) (the geometry of the contacts for the device marked by dashed lines). The positive and negative peaks of the current near the contacts and the reduced current in between indicate a photothermoelectric effect. The center of the channel can be located as the midpoint of the two peaks, where the PTE currents to both contacts are balanced. Carriers are generated at the laser-heated hot spot then diffuse to both contacts. The current measured between the contacts is the difference between the diffuse currents received by the two contacts. The carrier type can be determined by the polarity of the current when light is focused near the source or the drain. The pattern indicates PTE is dominant and the photovoltaic effect due to Schottky barriers at the metal-semiconductor contact is negligible. The I<sub>d</sub>-V<sub>d</sub> output characteristic showed that the contacts are Ohmic. A typical photocurrent under rotation of QWP angle  $\alpha$  is presented in Figure 3.1(c). The photocurrent vs. QWP angle  $\alpha$  of an 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se thin-film transistor under unbiased and ungated condition (V<sub>gs</sub> = 0 V, V<sub>ds</sub> = 0 V) is obtained by focusing the light at the center of the device. The results show a clear photoresponse to circular polarization originated from the spin-selective excitation and spin-momentum locking (will be further confirmed in later sections), however, accompanied by additional photocurrents originated from other mechanisms similar to the results reported in literature. (Duan et al., 2014; Huang et al., 2020b; Kastl et al., 2015; McIver et al., 2011; Pan et al., 2017) The photocurrent vs. QWP angle  $\alpha$  can be fitted by the sinusoidal function as expressed in Eq. 3.5.



Figure 3.1 Photocurrent in Bi<sub>2</sub>Te<sub>2</sub>Se thin film. (a) Schematics of experimental setup; (b) Photocurrent mapping of an 11-nm thick Bi<sub>2</sub>Te<sub>2</sub>Se device; (c) Photocurrent vs. polarization (QWP angle) of an 11-nm thick Bi<sub>2</sub>Te<sub>2</sub>Se device under  $V_{ds} = 0$  V,  $V_{gs} = 0$  V; (d) Schematics of the band structure of Bi<sub>2</sub>Te<sub>2</sub>Se and the photocurrents resulting from different mechanism.

$$J = D + C\sin 2\alpha + L_1\sin 4\alpha + L_2\cos 4\alpha \tag{3.5}$$

Here, the C term is the desired circular photoresponse for chirality detection. L<sub>1</sub> and L<sub>2</sub> are linear photoresponses and may be attributed to linear photogalvanic effect (LPGE) or photon drag effect due to lacking inversion symmetry at its surface states. (Olbrich et al., 2014; Plank et al., 2016a; Plank et al., 2016b) Both C and L terms are highly dependent on the intrinsic chemical potential,(Okada et al., 2016; Pan et al., 2017) which is sensitive to the surface condition. (Bahramy et al., 2012; Green et al., 2016; Kong et al., 2011) The polarization insensitive D term can be originated from photo-thermoelectric (PTE) and photovoltaic effect, (Besbas et al., 2016; Kastl et al., 2015; McIver et al., 2011; Yan et al., 2014) and are highly dependent on the location on the TI surface where the light interacts with. The photocurrent responds to both circular and linear polarized light as seen in the finite values of the fitted C (circular response) and  $L_1$  and  $L_2$ (linear response) terms in the inset of Figure 3.1(c). These additional photoresponses make it difficult to estimate the controllability of the TSS carrier transport using optical polarization. As illustrated in Figure 3.1(d), in the cases with larger  $L_1$ ,  $L_2$  terms (here we sketched the case of  $L_1$ ~ C), the photoresponses between ~  $60^{\circ} < \alpha < \sim 120^{\circ}$  are mostly due to linear polarization, and the polarity of the photocurrent is opposite to the spin-momentum locking current induced by the left/right circular polarization (LCP, RCP) incidence (the dashed section of the black curve flips the polarity to the opposite side of the baseline).

The photocurrent is measured and fitted using Eq. 3.5 for Bi<sub>2</sub>Te<sub>2</sub>Se devices with different thicknesses. The fitted parameters are shown in Figure 3.2. It is noticed that the polarity of circular polarization induced shift current (C) is consistent throughout the devices, despite the variation of the magnitude. However, both the magnitude and the sign of the L<sub>1</sub> and L<sub>2</sub> terms are indeterministic. The shift current can be attributed to TSS for both the sub-20-nm TSS-dominant devices and the thicker devices show more bulk contribution.(Luo et al., 2018) The linear-polarization dependent terms L<sub>1</sub>, L<sub>2</sub> depend on the angle between linear polarization direction and lattice orientation (will be shown later), which is random during device fabrication. Limited by the small size (typically  $10 \times 20 \ \mu m^2$ ), it is challenging to determine the lattice orientation (e.g., XRD usually requires several or tens of mm<sup>2</sup>) before device fabrication. This explains the indeterministic signs and relative magnitudes of L<sub>1</sub> and L<sub>2</sub>, i.e., the phase of azimuthal angle of LPGE current arctan(L<sub>2</sub>/L<sub>2</sub>). On the other hand, the absolute magnitudes of circular and linear photocurrent are related to the intrinsic chemical potential on its surface and will be discussed based on its gate-

tunability in Section 3.3. The variation of the polarization-insensitive photocurrent (D) is from photo-thermoelectric and/or photovoltaic effect(s) that is not eliminated at the center of non-perfectly symmetric devices.



Figure 3.2 Photocurrent components of  $Bi_2Te_2Se$  devices with different thicknesses, measured at  $V_{gs} = 0 \text{ V}$ ,  $V_{ds} = 0 \text{ V}$ , incident laser power ~ 0.5 mW focused at the center of the device.

A separate experiment is conducted to study the origin of the linear polarization-dependent  $\sin(4\alpha)$  and  $\cos(4\alpha)$  photocurrents. The  $\sin(4\alpha)$  and  $\cos(4\alpha)$  terms obtained from the photocurrent measurement by rotating the quarter waveplate has been observed in previous photocurrent measurements in similar material systems. These measurements showed that, in addition to the galvanic current driven by circular polarization, there are also responses of certain types of carriers to the rotation of linear polarization. Two possible mechanisms have been proposed, namely the linear photogalvanic effect (direction of current depends on electrical field direction only) and the photon drag effects (direction of current depends on both electrical field and Poynting vector directions) (Olbrich et al., 2014; Plank et al., 2016a; Plank et al., 2016b).

A simple treatment is adopted to handle both effects, considering only the second-order electrical field effect is linear within the measuring range of incident power (Glazov & Ganichev, 2014):

$$j_{\lambda} = \sum_{\mu,\nu} \chi_{\lambda\mu\nu} E_{\mu} E_{\nu}^{*} + \sum_{\mu,\nu,\xi} \psi_{\lambda\mu\nu\xi} E_{\mu} E_{\nu}^{*} q_{\xi} + o(E^{2+})$$
(3.6a)

$$\begin{bmatrix} j_{x} \\ j_{y} \end{bmatrix} = \begin{bmatrix} -\cos(2\alpha - 2\phi)\left(\chi - T_{z}q + \frac{T_{\parallel}q\theta^{2}}{2}\right)t^{2}E_{0}^{2} \\ \sin(2\alpha - 2\phi)\left(\chi - T_{z}q + \frac{T_{\parallel}q\theta^{2}}{2}\right)t^{2}E_{0}^{2} \end{bmatrix}$$
(3.6b)

where  $j(\vec{r}, t)$  is the electrical current density and  $E(\vec{r}, t)$  is the electrical field. The expansion coefficients  $\chi_{\lambda\mu\nu}$ , and  $\psi_{\lambda\mu\nu\xi}$  are 3<sup>rd</sup> and 4<sup>th</sup> rank tensor, respectively, describing the lattice structure and orientation.  $E^*$  is the complex conjugate of the *E* vector. *q* is the momentum vector of the incident light. Thus, the first term represents the photogalvanic effect that depends only on the electrical field direction, and the second term represents the photon drag effect that also depends on the direction of the wave vector of the incident light. For oblique incidence, it can be expressed as Eq. 3.6b (Plank et al., 2016b).

The origin of the linear polarization-dependent photocurrent is studied by rotating the device by 180 degrees while keeping the optical setup unchanged, so that the projection of the wavevector is reversed while the in-plane electromagnetic field magnitude remains the same. Here we repeat the photocurrent measurement with a half waveplate (HWP) to rotate the polarization direction. The linear polarization at HWP angle = 0 is also perpendicular to the channel. As shown in Figure 3.3(a), the variations of photocurrent vs. HWP angle are the same, showing the contribution from the linear photogalvanic effect, i.e., the dependence on the incident light polarization alignment with the lattice orientation. The discrepancy of the absolute value is inevitable due to the difficulty in aligning the laser focal spot at the exact same location. The photon drag effect plays a smaller role. This result also agrees with the microscale origin (Plank et al., 2016b) for which the photon drag requires a much larger sample to pronounce. In fact, all the reported observations of dominant photon drag currents so far are in bulk or chip-sized epitaxial samples.(Ganichev & Prettl, 2007; Plank et al., 2016a)

The linear photogalvanic effect can be attributed to the angle of the lattice orientation with respect to in-plane electromagnetic oscillation. The classical treatment above requires the lattice to have a broken inversion symmetry so that the linear photogalvanic effect, i.e., the  $\chi$  term to be finite. For the Bi<sub>2</sub>Te<sub>2</sub>Se lattice we studied, the bulk follows a  $D_{3d}$  group preserving the inversion symmetry while its surface is described by the  $C_{3v}$  group which lacks inversion symmetry. This means the L<sub>1</sub> and L<sub>2</sub> terms originate from the surface state. Generally speaking, the second-order effects result from the redistribution carriers in k-space under optical excitation, instead of polarization of the matter. The DC current originated from the optical oscillating field can be

microscopically explained by the asymmetric scattering of the carriers by the inversion-broken lattice potential. As shown in Figure 3.3(b) below, for the lattice (bulk) preserving inversion symmetry (left), the scattering is symmetric resulting in no net current. However, in an inversionsymmetry-breaking lattice (surface), carriers may lose more momentum when scattered with the lattice potential in the inversed direction, accumulated to generate a net current flow (Olbrich et al., 2014). The linear-polarization dependent terms  $L_1$  and  $L_2$  depending on the angle between linear polarization direction and lattice orientation, which is random during device fabrication, is verified.



Figure 3.3 (a) Photocurrent varying with polarization of light controlled by half-waveplate, oblique incident from two opposite direction (forward / backward). (b) Microscopic picture of the linear photogalvanic effect, of the bulk (left) inversion symmetry preserving states (e.g., C<sub>6v</sub> group), and surface (center and right) inversion-symmetry-breaking states (C<sub>3v</sub> group). The black double-headed arrows denote the polarization of the incident light, the blue arrows denote the net flow of the majority carriers.

Now, the mechanisms of different photocurrent components were reviewed, and the measurements of polarization-controlled photocurrents were presented. The results confirmed the existence of CPGE from TSS, also the LPGE origin. In the next two sections, three knobs, namely

the gate-voltage, bias voltage, and optical wavelength, are used to study and maximize the helical photoresponse.

#### 3.3 Helicity-Control under Electrical Gating: Deep Tuning of Photothermoelectricity

To explore the maximum helical-controllability, a back-gate voltage is applied onto thinfilm  $Bi_2Te_2Se$  devices to obtain an optimum chemical potential that TSS-related transport phenomena dominate. The photocurrent in the 11-nm device (same as the one in Figure 3.1) under varied gate voltage is measured and plotted in Figure 3.4. The condition that maximizes the CPGE current is found to be ~ -12 V. Two-terminal resistances of the device *R* vs.  $V_{gs}$  are also plotted in Figure 3.4, illustrating the chemical potential in the 11-nm film is effectively tuned by the backgate (the depletion layer thickness at this back gate voltage is ~30 nm (Huang et al., 2020b)). The peak of the resistance corresponds to the approximate location of the charge-neutral point (CNP), where the optimized condition for circular polarization detection is also located. The reason is that the chemical potential near CNP provides a minimum Coulomb blockade during the spin-selective excitation. As the chemical potential moves towards the bulk bands, the increased rate of scattering out of TSS also contributes to the drop of the circular photoresponse.



Figure 3.4 Photocurrents and device resistance vs. gate voltage under an incident power ~ 0.5 mW.

In the further studies below, a 1550-nm laser is selected to avoid the additional excitation of the Si 1.1 eV) semiconductor gate. The gate-tunability of PTE is first studied to understand the baseline, i.e., the large polarization-insensitive current. The laser spot is first scanned across the channel of an 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device. The photocurrent pattern is shown in Figure 3.5(a). The carrier type can be determined as n-type by the polarity of the current when light is focused near the source or the drain (left is source and right is drain in Figure 3.5(a)). We also measured the sheet resistance of the device with different back-gate voltages as shown in Figure 3.5(b). The decrease of the sheet resistance vs. back-gate voltage also indicates the n-type carrier, and the monotonic decrease indicates that the Fermi level is always above the Dirac point at all back gate voltages used in the experiment as illustrated in the band structure shown in the inset of Figure 3.5(b).(Luo et al., 2018; Xu et al., 2014) (Absolute value of the Seebeck coefficient is used in the discussion below since the sample is always n-type) The peak of the current at the source contact (position A in Figure 3.5(a)) is selected to extract the Seebeck coefficient for maximum signal.



Figure 3.5 (a) Photocurrent of incident light (1550-nm polarized perpendicular to the current) focal spot located along the channel. Location A and B are also marked. (b) Gate-dependent sheet resistance of the 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device. Inset: Schematics of the band structure of the Bi<sub>2</sub>Te<sub>2</sub>Se topological insulator. Intrinsic Fermi level is within the bandgap and above the Dirac point, negative gating brings the Fermi level down to around but above the Dirac point, and positive gating raises the Fermi level up to accessing the bulk band/Rashba states.

The Seebeck coefficient (*S*) is extracted using the temperature rise and the short-circuit current by laser heating. The short-circuit Seebeck current is directly taken from the polarization-

insensitive photocurrent term (details of the photocurrent will be given later). We measured thinfilm Bi<sub>2</sub>Te<sub>2</sub>Se properties including: optical absorption coefficient of  $1.37 \times 10^6$  m<sup>-1</sup> in 1550-nm (Venuthurumilli et al., 2019) and absorptivity in 633-nm is directly measured to be 26%; electrical property (electrical conductivity extracted from Figure 3.5(b)  $\sigma = 1/R_{sheet}t$ , where the contribution of the contact resistance is typically < 300  $\Omega$ , and is thus neglected in the calculation); and thermal conductivity of 2.3 W/m·K, (Luo et al., 2018), and then used a numerical model to find the temperature rise. The temperature rise is then coupled to a thermoelectricity model consisting of Seebeck voltage, Ohm current, Peltier heat flow, and Joule heating, to extract the Seebeck coefficient by matching the calculated short-circuit current with the measured value.

We first measure the Seebeck coefficient resulted from the photo-thermoelectric effect using linearly polarized light, hence, without spin injection, under different back-gate voltages. Our previous Hall effect measurements in Section 2.2 (Luo et al., 2018) showed that the 2D carrier density of sub-20-nm Bi<sub>2</sub>Te<sub>2</sub>Se thin films is ~1×10<sup>13</sup> cm<sup>-2</sup>, which is attributed to the TSS (5×10<sup>12</sup> cm<sup>-2</sup> each surface), and the bulk carrier concentration is less than  $2\times10^{12}$  cm<sup>-2</sup>. Estimation of Fermi level shifting, and bulk depletion depth can be made using the MOS capacitance model.

$$V_g = \psi_s + \frac{\varepsilon_{body}}{\varepsilon_{ox}} t_{ox} \sqrt{\frac{2eN}{\varepsilon_{body}}} \psi_s$$
(3.7a)

$$W_d = \sqrt{\frac{\varepsilon_{body}\psi_s}{eN}}$$
(3.7b)

Here,  $\psi_s$  is the surface potential, representing the Fermi level shift;  $\varepsilon$  is the dielectric constants for oxide layer (ox) and the channel material Bi<sub>2</sub>Te<sub>2</sub>Se (body), respectively; *e* is the electron charge, *N* is the bulk carrier concentration; and *W*<sub>d</sub> is the depletion layer thickness. Solving the two equations using  $\varepsilon_{body} \sim 113$  of Bi<sub>2</sub>Se<sub>3</sub> (Madelung, Rössler, & Schulz, 1998) and  $N \sim 2\times10^{12}$  cm<sup>-2</sup> extracted from Hall effect measurements of an 11-nm and a 16-nm Bi<sub>2</sub>Te<sub>2</sub>Se device(Luo et al., 2018), under 20 V gating, the depletion depth is found to be ~32 nm and the bottom Fermi level is shifted by ~0.5 eV. Thus, the entire film including the top surface of our 11-nm thin-film device can be effectively tuned by the back-gate. The measured Seebeck coefficient is plotted against the gate voltage in Figure 3.6(a) ( $\sigma = 0$ ). This Seebeck coefficient decreased from 147  $\mu$ V/K at large (V<sub>gs</sub> = -30 V) negative gating to 112  $\mu$ V/K when Fermi level moved towards the conduction band, then slightly increased to 116  $\mu$ V/K (V<sub>gs</sub> = -30 V). The non-monotonic

relation of the Seebeck coefficient and Fermi level indicates an interplay of different types of carriers.

The measured Seebeck coefficient mainly originates from the TSS carriers. This origin of the thermoelectric effect can be analyzed using the Landauer formalism. Unlike electrical conductivity or electronic thermal conductivity which depends much on the exact band structure, the Seebeck coefficient is only weakly affected by the details of band-structure and effective mass. For example, for all n-type bulk semiconductors with a parabolic band, the Seebeck coefficient vs. Fermi level relation falls on the same curve despite the difference in effective mass. (Jeong et al., 2010; Kim et al., 2009) Different Seebeck coefficient is only a result of different dimensionality (e.g., 2D electrons at the surface vs 3D electrons in the bulk) and the scattering rate, which can be calculated from the density of state. Hence the single band Seebeck coefficient of the TSS can be estimated using the Landauer formalism for 2D electron states with linear dispersion (Section 1.4)



Figure 3.6 Gate-tunable thermoelectric performance of the 11-nm thin-film  $Bi_2Te_2Se$  device, with helicity controlling (a) (Absolute value of) Seebeck coefficient (*S*) measured under zero spin injection ( $\sigma$ =0), and the extracted Seebeck coefficient using the total photocurrent measured under circularly polarized light ( $\sigma$ =±1). (b) Seebeck coefficients of 2D linear dispersion (solid blue line) and 3D parabolic dispersion (dotted black line) electron systems vs. normalized Fermi level calculated by the Landauer formalism.

For a given dimensionality (e.g., 3D bulk state or 2D surface state) and dispersion (e.g., parabolic for most single band semiconductors, linear for Dirac cone systems, etc.), the density of states and group velocity can be directly obtained, and the scattering rate  $(1/\tau)$  can be assumed to

be proportional to the density of states. Furthermore, the details of effective mass, degeneracies, etc. in  $L_{11}$  and  $L_{12}$  are canceled out so that for semiconductors with the same type of dispersion and dimensionality, the Seebeck coefficient at a given Fermi level is the same. For example, for 3D electrons with parabolic dispersion, DOS ~  $(E-E_c)^{1/2}$  and  $v \sim (E-E_c)$  so that the Seebeck coefficient is expressed by Eq. 3.8a (Jeong et al., 2010), in which k<sub>B</sub> is the Boltzmann constant,  $\eta_{F,C} = (E_F-E_c)/k_BT$  is the normalized Fermi level at temperature *T*, with respect to the conduction band edge, and  $F_i$  is the i-th order Fermi integral. Similarly, for the TSS with 2D surface states and linear dispersion, DOS is linearly dependent on  $(E-E_D)$  and group velocity is constant, the Seebeck coefficient can be estimated by Eq. 3.8b. Notice here  $\eta_{F,D} = (E_F-E_D)/k_BT$  is the normalized Fermi level from the Dirac point.

$$S_{3D,para} = -\frac{k_B}{e} \left[ \frac{\left(\frac{5}{2}\right) \mathcal{F}_{\frac{3}{2}}(\eta_{\rm F,C})}{\mathcal{F}_{\frac{1}{2}}(\eta_{\rm F,C})} - \eta_{\rm F,C} \right]$$
(3.8a)

$$S_{2D,linear} = -\frac{k_B}{e} \left[ \frac{3\mathcal{F}_2(\eta_{\rm F,D})}{\mathcal{F}_1(\eta_{\rm F,D})} - \eta_{\rm F,D} \right]$$
(3.8b)

Considering the possible Fermi level, the calculation results in Figure 3.6(b). Similarly to calculations in Ref. (R. Kim et al., 2009), the Seebeck coefficient generally decreases with normalized Fermi level for both 3D and 2D electrons. The theoretical result shows that the Seebeck coefficient of 2D electrons is in the range 80-160  $\mu$ V/K. The measured Seebeck coefficient, ~120  $\mu$ V/K, falls in this rage. On the other hand, the Seebeck coefficient of the parabolic 3D electrons in bulk is greater than 220  $\mu$ V/K when the Fermi level is below the band edge, much larger than the measured Seebeck coefficient. Therefore, it can be concluded that in this thin film, TSS electrons are the dominant carrier for temperature-driven electrical transport. The large contribution from TSS to the Seebeck coefficient under laser heating is also recently reported in Ref. (Nivedan et al., 2020). It has also been reported that under controlled Fermi level and scattering, TSS dominance could improve the power factor,(Hsiung et al., 2015) also, a TSS dominant conduction but bulk dominating Seebeck effect can be achieved.(Guo et al., 2016; Zhang et al., 2015) Notice this discussion also explains the slight increase at very large positive gating, i.e., the conduction band kicked in as its carrier density increased.

In addition, we directly measured the Seebeck voltage and local temperature using micro-Raman thermometry under a 633-nm laser normal incidence to validate the Seebeck coefficient extraction. During those measurements when there is laser irradiation at an oblique angle to generate photocurrent, the micro-Raman thermometry for temperature measurement cannot be applied due to limited spacing. To validate the Seebeck coefficient extraction procedure described in the main text, we measured the photo-thermoelectric (Seebeck) voltage with a direct local temperature rise measurement using micro-Raman thermometry at normal incidence(Luo et al., 2014). The Seebeck coefficient is calculated from the temperature and the measured Seebeck voltage using  $V_s = \Delta \Phi = S\Delta T$ . The open-circuit Seebeck voltage of the device is directly measured (Keithley Source Meter 2612). The focused laser locally heats up at the contact to obtain maximum Seebeck voltage signal, and induces a Raman scattering shift. The temperature-dependent Raman shift of  $E_g^2$  mode is calibrated as the temperature transducer ( $\chi_{\theta} = 0.015$  cm<sup>-1</sup>/K) (Luo et al., 2018). The same numerical model is used in the validation. The properties of Bi<sub>2</sub>Te<sub>2</sub>Se are included in all the physical models. The contact metal is included in all other processes except for the Seebeck effect due to the small Seebeck coefficient and small temperature gradient. The SiO<sub>2</sub>/Si substrate and ambient air are only considered in the heat transfer model. The temperature rise for the validation is also calculated in this model using open-circuit electrical boundary condition instead of the short-circuit condition used in the main text, and is compared to the measured temperature rise using micro-Raman thermometry. Figure 3.7 shows details of the Raman thermometry measurement. At a given incident power, the Raman shift of the  $E_g^2$  mode is measured to find the temperature rise, and is compared with the heat transfer modeling result (Figure 3.7(a)). Figure 3.7(b) shows the measured open-circuit voltage vs incident power and the temperature rise. The temperature rise obtained from modeling is lower than that measured using Raman thermometry by about 15%, mainly due to the errors propagating from optical properties and thermal conductivity measurements. This systematic error is corrected in the Seebeck coefficient shown in Figure 3.6.



Figure 3.7 Extracting Seebeck coefficient from temperature rise and thermoelectric voltage. (a) Temperature rise under varied incident laser power by heat transfer modeling and Raman thermometry measurement. (b) Temperature rise vs. laser power when laser spot at a contact and the corresponding open circuit Seebeck voltages.

Now we use circularly polarized incident light and repeat the photocurrent measurement to study the photo-thermoelectric effect with optical spin-injection. In addition to the optical heating, the right/left-handed circular polarization ( $\sigma = \pm 1$ ) simultaneously inject up/down spin polarization to the TSS, so that the preferred motion of the excited TSS is parallel/antiparallel to the carrier flow driven by the temperature gradient, respectively, due to the spin-momentum locking. The same temperature rise is achieved when the incident light is circularly polarized, while the resulted electromotive force is tuned by the additional TSS current from spin injection. Thus, we adopt the thermoelectricity framework here to present the result of carrier diffusion that is driven by the spin current in addition to the temperature gradient in terms of the thermoelectric property, i.e., an apparent Seebeck coefficient. The measured photocurrent is subsequently used to extract the apparent Seebeck coefficient using the model presented above assuming the same temperature distribution, and is also plotted in Figure 3.6(a) to compare with results without optical spin injection ( $\sigma = 0$ ). Under right-handed circular polarization ( $\sigma = +1$ ), the extracted Seebeck coefficient rises to 248  $\mu$ V/K when a 30 V negative gate voltage is applied, 60% more than that without spin injection under the same gate voltage (147  $\mu$ V/K at V<sub>gs</sub> = -30V). As the gate voltage is increased to positive, the Seebeck coefficient drops. Interestingly, the drop is much steeper than that when  $\sigma = 0$ , down to 84  $\mu$ V/K at V<sub>gs</sub> = +30V, below the value for  $\sigma = 0$  (116  $\mu$ V/K). Hence, the optical spin injection broadens the tuning range of the Seebeck coefficient  $S_{max} - S_{min}$  by more

than five times, or ratio  $S_{\text{max}}/S_{\text{min}}$  by more than twice throughout the range of gate voltage. Similarly, under left-handed circular polarization ( $\sigma = -1$ ), the optical spin injection of TSS that moves antiparallelly to the temperature-driven carrier flow suppresses the photo-thermoelectric current when a zero and negative gate voltage is applied, and enhances the photo-thermoelectric current under large positive gating. The apparent Seebeck coefficient of  $\sigma = -1$  presents an opposite trend from that with zero and  $\sigma = +1$  spin-injection, increasing from 90 to 170  $\mu$ V/K with gate voltage, and the tuning range and the ratio are also much larger than the case without spin injection. It is also noticed that, when the Fermi level is deep into the bandgap ( $V_{gs} = -30V$ ), the photothermoelectric current driven by the incident light with different polarization can differ by as much as five times. Hence, the combination of the optical helicity and electrical gating can significantly tune the photo-thermoelectric current in thin-film  $Bi_2Te_2Se$  devices, and this the large tunability of the Seebeck coefficient where TSS is dominant in thermoelectric transport offers a possibility of realizing thermal energy devices using helicity-controlled heat carriers.

The large tunability of the Seebeck coefficient is originated from the large tunability of the helicity induced current. Now the laser focal spot is moved to the center of the device (location B in Figure 3.5(a)) where the photo-thermoelectric current towards the two contacts is balanced.

Figure 3.8(a) shows that the photocurrent vs. QWP angle evolves with the back-gate voltage when the Fermi level is tuned to access different parts of the electron band. At zero and negative gate voltage, a clear helicity dependent photocurrent is observed following the  $sin(2\alpha)$  trend (Eq. 3.5), indicating the *C* component is dominant. This circular photocurrent is driven by the angular momentum selection rule of the spin-momentum locked topological surface states under helical incident light. (The current polarity is the same as the enhancement/reduction of the photo-thermoelectric effect and agrees with the spin selection of the optically injected angular momentum used in our experiment configuration.) The result is similar to earlier works (Duan et al., 2014; Kastl et al., 2015; McIver et al., 2011), while the magnitude of the helical current (both the absolute photo-response and the relative intensity of *C* to other components of the photocurrent L<sub>1</sub> and L<sub>2</sub>) is much greater due to the longer spin lifetime(Iyer et al., 2018) when the Fermi level is within the bulk bandgap.



Figure 3.8 Photocurrent components of the 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device under back-gating. (a) Photocurrent vs. quarter waveplate curves at varied gate voltage. The focal spot is located at the center of the channel. (b, c) Polarization-dependent components under varied gate voltage, with the focal spot at the center (b) and at the left contact (c). L<sub>1</sub> and L<sub>2</sub> are multiplied by a factor of 5 for clarity. D denotes the polarization-insensitive component of photocurrent; C is the circularpolarization-dependent photocurrent; L<sub>1</sub>, L<sub>2</sub> are the circular-polarization-dependent photocurrent; C0 is the fitting coefficient of the  $cos2\alpha$  term, i.e., artifacts due to measurement uncertainties.

The fitted components of the polarization-dependent photocurrent are plotted against the gate voltage in Figure 3.8(b) to show the field effect more clearly. Negative gating depletes electrons, and the Fermi level is tuned lower, away from the conduction band edge and towards the Dirac point (Figure 3.5(a) inset), reducing both Pauli blocking by opening up more TSS available for excitation from the valence band, (Bao et al., 2009; Mikhailov & Ziegler, 2007) also possibly reducing the scattering with spin-degenerated states in the conduction band that causes spin depolarization. (Bahramy et al., 2012) Both effects result in a larger photocurrent as shown in Figure 3.8(b). Despite the reduction of the density of states near the Dirac point, the photogenerated carrier density is not much affected due to the relatively low pumping rate of the incident light and the fact that the photon energy (~0.8 eV) is much larger than the bandgap (~0.3 eV). Using the irradiation intensity and surface state absorption (~2% for one surface),(Venuthurumilli

et al., 2019) the carrier generation rate is estimated to be below  $10^{21}$  cm<sup>-2</sup>s<sup>-1</sup> with the quantum efficiency not exceeding unity. Together with the ~10 ps carrier lifetime (Iyer et al., 2018), the excited carriers density is below  $10^{10}$  cm<sup>-2</sup>, less than 0.2% of the carrier density on one surface. This excited carrier density also includes the valence band to conduction band transition. Hence the actual excitation density involving TSS is even smaller.) When a large enough positive gating is applied, we observe that the circular photocurrent is sharply reduced to zero and then flipped its sign. This is likely due to the spin-wise selection of the Rashba states created in the conduction band. (Bahramy et al., 2012; Zhang et al., 2010) These states possess an opposite spin-texture to that of the TSS (Bahramy et al., 2012; Hong et al., 2012; McIver et al., 2011; Zhang et al., 2010) and thus resulting in a helical current in the opposite direction. Additionally, there is another possible transition that cannot be easily ruled out. A second topological surface state (TSS-2) with similar Dirac-like dispersion has been found in Bi<sub>2</sub>Se<sub>3</sub>, ~1.5 eV above its intrinsic Fermi level. (Sobota et al., 2012) Bi<sub>2</sub>Te<sub>2</sub>Se is expected to share a similar band structure, but the exact energy level of TSS-2 is yet to be studied. The transition from the conduction band to the TSS-2 below the Dirac cone, which has a negative group velocity, may also result in the inversed helical current.

Another thin-film 13-nm Bi<sub>2</sub>Te<sub>2</sub>Se device tested to scrutinize the gate-dependent CPGE is presented in Figure 3.9. An intermediate near-flat terrain is observed around  $V_g = 0$  V, which also happened to be around the "OFF-region" for CPGE. A tentative argument is that, the responses from TSS and Rashba states coexist and cancel each other, and the TSS has a stronger net effect due to the longer relaxation time despite the lower density of states. However, it requires further studies using other techniques, e.g., photo-Hall effect measurement identifying the dominant carriers.



Figure 3.9 Photocurrent components of a 13-nm Bi<sub>2</sub>Te<sub>2</sub>Se device under back-gating. (a) Photocurrent vs. quarter waveplate curves at varied gate voltage. The focal spot is located at the center of the channel. (b) Polarization-dependent components under varied gate voltage, with the focal spot at the center.

The magnitudes of the sin/cos(4 $\alpha$ ) terms, denoted by L<sub>1</sub> and L<sub>2</sub>, are also obtained by fitting the curves to Eq. 3.5, which are caused by linear photo-galvanic effect due to its dependence on the rotation of the linear polarization as discussed in Section 3.2. From Figure 3.8(b) we can also notice a slight increase of linear polarization-dependent photocurrent (the magnitude of L<sub>1</sub>, L<sub>2</sub>) with increasing positive gate voltage. This increase is due to the Fermi level approaching the conduction band. Conversely, under negative V<sub>g</sub>, the Fermi level recesses deeper into the bulk bandgap so the contribution from the topologically trivial states in the conduction band is reduced. The measured linear photo-galvanic components reduce to a finite number but not zero. This indicates that both the topological surface state and the trivial state due to the band bending contribute to the linear-polarization-dependent photocurrent. A persisting linear-polarizationdependent photocurrent associated with the helical photocurrent is also observed in previous works. (Kastl et al., 2015; McIver et al., 2011)

The gate-dependence of each component of photocurrent is also compared with the results when the laser is focused at position A (Figure 3.8(c)). The circular photocurrents exhibit almost the same trend of gate-dependence at both locations, indicating the conclusion obtained at the center of the device that a clear helical photocurrent and accompanied linear responses are gate-controllable per the accessed electronic states, is also valid for that at the contact. Compared to the result at the center of the device, the helical current at the contact is nearly four times larger, which is due to the finite diffusion length of the spin. In fact, the ratio of the helical photocurrent magnitude at the center and the contact of the 6-µm channel can be used to estimate spin diffusion length L<sub>s</sub>, which turns out to be ~ 5 µm assuming exponential decay of helical photocurrent magnitude vs. distance (*x*) between the laser spot and the contact  $C_{center}/C_{contact} = C(x)/C(0) = \exp(-x/L_s)$ . This spin-diffusion length agrees with our previous ultrafast pump-probe measurement of the spin lifetime (a few 10s of ps) (Iyer et al., 2018) and magneto-transport measurement of the Fermi velocity (1-2×10<sup>5</sup> m/s),(Cao et al., 2014) which give a spin diffusion length on the order of a few micrometers.

Thicker (27 nm and 74 nm)  $Bi_2Te_2Se$  devices are also studied using the same approach to further understand the mechanism when more bulk state carriers are involved as the film thickness is increased. (Luo et al., 2018; Xu et al., 2014) The results are shown in Figure 3.10. Noticed that the majority carrier type is p-type for the much thicker 74-nm device, which can be clearly observed from the field-effect transport curve (Figure 3.10(a)) and the photo-thermoelectric pattern (Figure 3.10(b)). Now that the bulk carriers are dominant in the 74-nm  $Bi_2Te_2Se$  film, the intrinsic Fermi level is close to the valence band, which agrees with our previous Hall effect measurement for thick film and bulk  $Bi_2Te_2Se$ . (Cao et al., 2014; Luo et al., 2018)

The Seebeck coefficients are also extracted for the 27-nm and 74-nm devices (Figure 3.10(c)), ~-300 and 400  $\mu$ V/K respectively. Based on the analysis based on Landauer formalism shown in Figure 3.6(b), the dominant carriers are from the bulk band since the absolute values of Seebeck coefficients are greater than 220  $\mu$ V/K. In the 27-nm film, the band-bending due to surface oxidation (shown by ARPES (Cao et al., 2014)) is expected to form an inversion layer with conduction band electrons and show an averaged n-type behavior in the entire film. From the results observed in devices with different thicknesses, the surface band-bending plays an important

role that affects which type of carriers dominates. Thus, special precautions, including but not limited to thickness control(Luo et al., 2018; Pettes et al., 2013) and surface chemistry(Walsh et al., 2017; E. Wang et al., 2015), are needed in fabricating tetradymite-based TI devices with desired performance.



Figure 3.10 Field-effect tunability of helical and photo-thermoelectric current in 27-nm and 74-nm Bi<sub>2</sub>Te<sub>2</sub>Se films. (a) Sheet conductance at varied gate voltage. (b) Photocurrent of incident light vs. focal spot location along the channel. (c) Seebeck coefficient extracted using the polarization insensitive component of the photocurrent. (d) Helicity-tuned Seebeck coefficient extracted using the helical photocurrent.

As shown in Figure 3.10(d), in the 74-nm film, the abundant bulk carriers screen the top TSS from the back gating and the helical photocurrent is not tuned effectively. For the 27-nm device, there is some observable tuning when positive gating brings the Fermi level to the TSS warping region, but helicity-control is less effective compared to the 11-nm film shown in the main text, and back gating is not sufficient to turn off the thermoelectric effect completely.

To conclude Section 3.3, the experiment showed highly effective helicity control of topological surface states under electrical field gating, and the contribution of the helicity controlled TSS to electro-thermal transport. The helical photocurrent is amplified when the Fermi level is deep in the bandgap approaching the Dirac cone when Pauli blockage and spin-depolarizing scattering are reduced. On the other hand, the helical photocurrent is diminished when the Fermi level is close to the conduction band edge and is even inverted when accessing the conduction band Rashba states. As a result, the photo-thermoelectric current can differ by as much as five times depending on the polarization of the heating laser, and the gate tunability of the photo-thermoelectric current can also be broadened by more than five times. These results showed the potential for effective manipulation of topological surface states and building helicity-controlled optoelectrical and thermal devices.

### 3.4 Helical-Control under Electrical Bias: Circular Photoconductance for Optical Chirality Detection

In this section, bias voltages are applied in addition to the gate voltages to modulate the spininjected electrical transport under 633-nm, 1550-nm, and 10.6-µm laser incidence. Clear helicalcontrolled photocurrents are observed for both above and below bandgap excitation. A consistent response to circularly polarized light under bias voltages are also observed and understood as a helical photoconductance, while the photoconductance does not respond to linear polarization. Thus, the photoconductance is expected to be useful as a measure of circular polarization. The following content is reported in the context of optical chirality detection.

The photocurrent from circular polarization can be unambiguously separated from linear polarization by obtaining the differential photocurrent at different bias voltages, i.e., by subtracting the photocurrent under 0 V from that under 10 mV bias voltage in Figure 3.11(a).



Figure 3.11 (a) Photocurrent vs. polarization (QWP angle) of an 11-nm thick  $Bi_2Te_2Se$  device under  $V_{ds} = 0$  V and 10 mV,  $V_{gs} = 0$  V; (b) Differential photocurrent vs. polarization (QWP angle) of the 11-nm thick  $Bi_2Te_2Se$  device obtained with 0 and 10 mV bias.

The differential photocurrent shown in Figure 3.11(b) can be well-fitted using only two terms, the circular photoresponse  $C\sin 2\alpha$  and the polarization-insensitive D term. Hence, the differential photocurrent is sensitive solely to the circular polarization but not to the linear polarization. We attribute amplification of circularly polarization-dependent photocurrent under bias to the long spin-relaxation time of TSS electrons generated by circular polarized light. It has been found that optically injected spin polarization persists for over 10 ps, covering the entire energy relaxation process. (Iver et al., 2018) The differential photocurrent under circularly polarized excitation can thus be understood as a spin-dependent photoconductance due to photogenerated carriers with persisting spin polarization, in addition to the spin-momentum locked shift current at zero bias. On the other hand, the linear polarization-dependent photocurrent is not amplified by the bias because it is in essence an accumulation of momenta during high-frequency electromagnetic oscillation (Section 3.2), which is not affected by a DC voltage/current. The accumulation of electron momenta that leads to LPGE relaxes in a much shorter timescale (<100 fs) (Pettes et al., 2013) and thus only contributes to the photocurrent but not photoconduction. We found that the differential photocurrent solely depends on circular polarization for all the devices studied, with thicknesses of the devices ranging from  $\sim 10-70$  nm and the results will be showed after the optimum photoconductances are introduced.

In Figure 3.12(a), we show the photoconductance obtained at the bias of 10 mV ( $V_{gs} = -12$  V) against QWP angles, which can be fitted using  $G = G_D + G_C \sin 2\alpha$ . The maximum and

minimum values obtained at RCP (at  $\alpha = 45^{\circ}$ ) and LCP (at  $\alpha = 135^{\circ}$ ) are marked by blue and red vertical arrows. To improve the accuracy of the photoconductance measurement, especially the circular photoconductance  $G_c$  that is related to circular polarization detection, the photocurrent is measured at different bias voltages in I-V sweeps. In Figure 3.12(b), we show the photocurrent I<sub>d,ph</sub> from circular polarization (by subtracting the unpolarized component and the value at zero bias) vs. V<sub>ds</sub>, together with their linear fit for obtaining  $G_c$  (the dashed line). The I<sub>d,ph</sub>-V<sub>ds</sub> curve shows a good linear fit for  $G_c$ . The averaged uncertainty of the photoconductance as a measure for polarization can thus greatly improve the sensitivity compared with merely the differential photocurrent obtained at one V<sub>ds</sub> in Figure 3.11(b) and Figure 3.12(a).



Figure 3.12 Polarization dependent photoconductance in an 11-nm thickness BTS device. (a) Photoconductance vs. polarization (QWP angle), obtained by photo I-V sweep, with an incident laser power ~ 0.5 mW,  $V_{gs} = -12$  V; (b) Scaled photocurrent vs. bias voltage under RCP, LCP incidence. (c) Photoconductance and device resistance vs. gate voltage under an incident power ~ 0.5 mW; (d) Photoconductance components (G<sub>D</sub>, G<sub>C</sub>, G<sub>L1</sub>, G<sub>L2</sub>) vs. incident power, measured at  $V_{gs} = -12$  V.

The back-gate voltage also affects photodetection. The optimized condition for circular polarization detection is obtained by maximizing  $G_c$  vs. back-gate voltages, which is found to be ~ -12 V as shown in Figure 3.12(c). Two-terminal resistances of the device R vs.  $V_{gs}$  are also plotted in Figure 3.12(c), illustrating the chemical potential in the 11-nm film is effectively tuned by the back-gate (the depletion layer thickness at this back gate voltage is ~30 nm (Shouyuan Huang, Miotkowski, et al., 2020)). The peak of the resistance corresponds to the approximate location of the charge-neutral point (CNP), where the optimized condition for circular polarization detection is also located. The reason is that the chemical potential near CNP provides a minimum Coulomb blockade during the spin-selective excitation. As the chemical potential moves towards the bulk bands, the increased rate of scattering out of TSS also contributes to the drop of the circular photoresponse. In addition, the CNP is away from the trivial bands so PTE and LPGE effects are reduced. Therefore, the circular photoresponse is maximized near CNP. Photoconductance is further investigated with increased incident intensity. Figure 3.12(d) shows no sign of saturation till the maximum available power. The photoresponsivity of the (total) light intensity and CPL intensity are extracted to be 1.66 mA/W and 0.21 mA/W, respectively. The helical modulation of photoconductance under maximum available power (~4 mW) is  $G_c = 6.0 \,\mu\text{S}$ which is  $\sim 2.5\%$  of the total conductance.

The photoconductances are further extracted using I-V sweeps from the same batch of devices. The fitting results are obtained using the equation similar to Eq. 3.5,  $G = G_D + G_C \sin 2\alpha + G_{L_1} \sin 4\alpha + G_{L_2} \cos 4\alpha$ . The results showed in Figure 3.13 are measured at its optimized gate voltage chirality detection, and those of the sub-20-nm devices are plotted in Figure 3.13 inset (red). The photoconductance for thicker devices showed negligible gate dependence because the back-gate field effect is ineffective in tuning the chemical potential on the top surface. (Huang et al., 2020) The photoconductance is found to be only sensitive to circular polarization and insensitive to linear polarization rotation for all devices ranging 10-70 nm in thickness. The polarities of chirality-sensitive photoconductance of the devices are also consistent because of the same TSS origin.



Figure 3.13 Photoconductance components of Bi<sub>2</sub>Te<sub>2</sub>Se devices with different thicknesses, incident laser power ~0.5 mW focused at the center of the device. Inset, optimized gate voltages of sub-20-nm devices for chirality detection (red) and incident power measurement (blue).

The results shown above are obtained at the center of the device where the thermoelectric effect is minimum. However, photoconductance of circular polarization  $G_c$  is nearly uniform with a variation of less than 5% across the entire device as shown in Figure 3.14. Here, the differential photocurrents under 0 and 30 mV bias voltage  $G_{LCP}$  and  $G_{RCP}$  are obtained for both LCP and RCP incidences, and the differences of the two,  $G_c = \left[G\left(\alpha = \frac{\pi}{4}\right) - G\left(\alpha = \frac{3\pi}{4}\right)\right]/2$ , are mapped over the entire device. Photocurrent generated from PTE that has a large spatial variation is only weakly dependent on the bias voltage and is therefore canceled. This is because the PTE photocurrent depends on the temperature rise caused by laser heating but little on the bias. This indicates that circular photoconductance of TI transistors can be used to measure CPL with random shapes of the light beam and does not require focusing of the light beam to a certain location.



Figure 3.14 Mapping of the photoconductance contrast between LCP and RCP incidences.

Figure 3.12 provides the basis for characterizing the chirality of a light beam. To use a device for measurements, the polarization-insensitive photoconductance  $G_D$  and the chiralitysensitive photoconductance  $G_{\rm C}$  can be obtained to produce a power-dependent calibration chart (Figure 3.12(d)), which can be converted to the photoconductance per unit irradiation power.  $G_D$ and  $G_{\rm C}$  are then used to produce a photo-output characteristic graph similar to Figure 3.12(b) for a given incident power. When using the device for polarization measurement, Id,ph vs. Vds are measured which result in a line between the LCP (red) and RCP (blue) lines in Figure 3.12(b). The irradiation is partially LCP (RCP) if the measured line has a positive (negative) slope. The  $sin2\alpha$ behavior of circular polarization-dependent photoconductance (Figure 3.12(a)) indicates that the measured slope is proportional to the percentage of circular polarization. The degree of chirality, i.e., the percentage of circular component  $p_c = \frac{P_{CPL}}{P_{total}}$  of an elliptical polarized light beam can then be quantified using the ratio of the measured and calibrated slope. The aforementioned uncertainty of photoconductance (the slope of the curve) of 5.6% indicates that the chirality of a light beam with a circular polarization component larger than 5.6% can be discerned. Hence, this uncertainty can be defined as the chiral sensitivity for characterizing the performance of chirality detection. For comparison, metamaterial-based chirality detectors and circular polarization filters are often characterized by the circular polarization extinction ratio (CPER, the ratio of the transmissivity of one chirality to the other), and the inverse of CPER, 1/CPER also indicates the percentage of circular polarization above which the chirality can be discerned. Therefore, we can compare our uncertainty with 1/CPER. The reported metamaterial-based detection has reached a CPER = 35 i.e., chiral sensitivity  $\sim$ 3%. (Basiri et al., 2019) However, our device, using intrinsic physical properties of TI, requires much less effort in fabrication.

We also observed that circular photoconductance does not increase with the thickness of devices (Figure 3.13), excluding the bulk spin Hall effect contribution to the photoconductance (Seifert et al., 2018) and further confirming the TSS origin. The spin potentiometry measurements on  $Bi_2Te_2Se$  thin films (Tian et al., 2017, 2019) also revealed the TSS contribution is much greater than that of the bulk spin Hall effect.

Because the origin of the circular photoconductance is the TSS with gapless Dirac dispersion, the chirality detection can also operate under lower energy excitation and even in mid-infrared (MIR) which can be used to directly measures the chiral thermal radiation from special texture or materials. (Chiou et al., 2008; Khan & Narimanov, 2019) Examples of chirality detection in telecom (1550-nm) and MIR (10.6- $\mu$ m) are presented below. Due to the high absorption of 10.6- $\mu$ m light in the oxide layer, the repeatability is largely impeded by the severe heating. Thus, undoped Si substrates are used only to show the concept, and the gate-dependence is not studied in detail.

Two-terminal Bi<sub>2</sub>Te<sub>2</sub>Se devices are fabricated on undoped Si substrates (same procedure as described earlier, Al<sub>2</sub>O<sub>3</sub> capping layer is skipped). The negligible shunning is verified by measuring a dummy sample with the same geometry. The resistance over the undoped Si in the dummy sample is >1MΩ, much larger than the typical resistance of a Bi<sub>2</sub>Te<sub>2</sub>Se device of a few kΩs (4.7 kΩ for the device showed below). A  $\lambda/4$  reflective phase retarder (RPR) is used to convert the linear polarization into elliptical/circular polarization. The circular component of the output beam from the RPR showed a sin(2θ) dependence of the incident polarization angle θ controlled by a wire-grid polarizer. The total power of the laser beam varies during the rotation of the polarizer. The raw photocurrent measurement can be corrected by measuring the power of the beam at every polarization angle to remove the polarization-insensitive photocurrent that only depends on incident power. The photocurrent measurement for a 22-nm device is shown in Figure 3.15(a). The corrected photocurrent can be well-fitted by  $J = C \sin(2\theta)$ . The photocurrent itself serves as a good candidate chirality detector.


Figure 3.15 Photocurrent vs. incident polarization angle to the reflective phase retarder in a 22nm Bi<sub>2</sub>Te<sub>2</sub>Se device measured at (a)  $V_{ds} = 0$  V and (b)  $V_{ds} = 30$  mV, under 10.6 µm laser incidence with power ~4 mW focused at the center of the device. (c) The differential photocurrent obtained from the photocurrent measured at  $V_{ds} = 0$  V and  $V_{ds} = 30$  mV. (d) Photocurrent vs. bias voltage under RCP and LCP incidence.

We further apply a 30-mV bias voltage and repeat the photocurrent measurement as plotted in Figure 3.12(b). The differential photocurrent is then obtained and plotted in Figure 3.12(c). Similar to the procedure described in the main text, chirality is detected using photocurrent I-V sweep and comparing with Figure 3.12(d). The measured I<sub>d,ph</sub>-V<sub>d</sub> curve for the irradiation with partially LCP (RCP) lies between the red LCP (blue RCP) curve and the black UP curve. The degree of chirality,  $p_c$  of the elliptically polarized light can be quantified using  $p_c = \frac{G_{measured}-G_D}{G_c}$ . The chiral sensitivity (~12-18%) and chiral-photoresponsivity (0.097 mA/W) are lower than the visible wavelength shown in the main text due to the low absorption in IR (Venuthurumilli et al., 2019) as well as not applying gate due to the use of undoped silicon. Our purpose here is just to show the possibility of using Bi<sub>2</sub>Te<sub>2</sub>Se phototransistor for chirality detection in a wide spectrum of wavelengths. The differential photocurrent of the same device using 1550-nm incidence is also measured and plotted in Figure 3.16. The chiral sensitivity is  $\sim$ 9.5% and the chiral responsivity is 2.44 mA/W. It is also extracted that the maximum modulation of photoconductance under available power are 0.93% and 0.62% respectively for 1550-nm and 10.6-µm lasers.



Figure 3.16 (a) Photocurrent vs. polarization (QWP angle) of an 22-nm thick  $Bi_2Te_2Se$  device under  $V_{ds} = 0$  V and 10 mV,  $V_{gs} = 0$  V, under 1550-nm laser incidence with power ~ 1 mW (b) Differential photocurrent vs. polarization (QWP angle) of the 22-nm thick  $Bi_2Te_2Se$  device obtained with 0 and 10 mV bias.

Figure 3.12(c) shows the circular photoconductance varies greatly with the back gate, from a peak value at  $V_{gs} \sim -12$  V to near zero when  $V_{gs} = 20$  V, due to the chemical potential moving from CNP to the conduction band edge. On the other hand, the polarization-insensitive component of photoconductance ( $G_D$ ) varies only slightly in a wide range of back-gate voltage from -20 V <  $V_{gs} < 20$  V. As discussed previously, the chemical potential resides in the bulk bandgap in this range of back-gate voltage. The photoconductance depends on the generated carrier density, which is determined by the product of optical absorbance and relaxation time. When the chemical potential resides in the bulk bandgap, the absorbance (optical transition rate) is proportional to the TSS density of states (DOS), while the relaxation time in TSS is inversely proportional to the DOS, (Pierret, 2003) resulting in a constant photoconductance. The constant photoconductance from non-polarized light and the varied photoconductance from polarized light provide a simplified approach in the measurement. When measuring a light beam with unknown intensity, we can first measure the (total) *G* at a large positive bias, e.g.,  $V_{gs} = 20$  V, which reflects the total irradiation intensity. This *G* is then subtracted from the total *G* measured under  $V_{gs} = -12$  V to obtain the circular component. This substitution of  $G_D$  (at  $V_{gs} = -12$  V) with *G* at  $V_{gs} = 20$  V enables measurement of chirality without the knowledge of the irradiation intensity, but at a cost of introducing a slightly larger uncertainty in obtaining  $G_c$  and a chiral sensitivity of ~10%. We found this strategy is applicable for devices with thickness below 15 nm. (Figure 3.13) The circular component photoconductance of sub-20-nm devices can similarly be switched off at positive backgate voltages as plotted in Figure 3.13 inset (blue). The corresponding polarization-insensitive photoconductance ( $G_{D0}$ ) is also presented in Figure 3.13. Approximating  $G_D$  using  $G_{D0}$  introduced ~< 10% uncertainty for the 9.5-13 nm devices, and 25% uncertainty for the 15-nm devices in chirality detection. Thicker devices are more challenging because the back-gate does not effectively tune the chemical potential throughout the thickness of the device. (Shouyuan Huang, Miotkowski, et al., 2020)

Lastly, we discuss using the same TI device for full polarimetry imaging so that to resolve the complete polarization states. We already showed in the photoconductance measurement that the total intensity (*I*, Eq. 3.4a) of the light beam, the intensity (or percentage) of the circular component (Eq. 3.4b), and the chirality can be obtained. When the light is elliptically polarized (a combination of linear and circular polarized light with a degree of polarization p = 1, Eq. 3.4c), the only remaining parameter is the orientation of linear polarization ( $\psi$ , Eq. 3.4d), since the amplitude of the linear polarization can be obtained from the difference between the total and circular polarization components.

The linear photogalvanic effect (LPGE) is used here to characterize the linearly polarized light. To obtain the optimized condition for linear polarization measurement, gate-dependent photocurrents are obtained and are shown in Figure 3.17(a). At a large positive gating,  $V_{gs} = 30$  V, the helicity-controlled photocurrent is completely turned off and thus it is an ideal condition for linear polarization detection. This is because the chemical potential is tuned to the warping region at the conduction band edge where the spin texture is not strictly locked to momentum. (Bahramy et al., 2012) Also, the electrons are easily scattered to spin-degenerated states. (Bahramy et al., 2012; Shouyuan Huang, Miotkowski, et al., 2020) On the other hand, the trivial state due to the band-bending on the surface is further filled with the increase of the back-gate voltage, thus the LPGE signal is increased. The photocurrent resulting from linear polarization incidence is plotted vs. the angle of the QWP  $\alpha$  or half the polarization angle  $\psi$  in Figure 3.17(b) and shows a clear

linear polarization dependence that can be expressed as a function of  $J = 35.5\cos(4\alpha+0.16\pi) = 35.5\cos(2\psi+0.16\pi)$  nA. An angle of  $0.16\pi$  exists in the fitted function because photoresponse from linearly polarized light is related to the lattice orientation as discussed in Section 3.2, and the *a*-axis of the lattice is not intentionally aligned with the channel during fabrication. This angle can be easily calibrated with measurements shown in Figure 3.17(b). The measured current is then used for determining the polarization angle  $\psi$ , which can be plug into Eq. 3.4 (a-d) to find the Stokes parameters S<sub>0-3</sub>.



Figure 3.17 Linear polarization photocurrent response in an 11-nm thickness BTS device. (a) Photocurrent components vs. gate voltage under an incident power ~ 0.5 mW; (b) Photocurrent vs. polarization (QWP angle) in the radial coordinate, measured at the device center, with an incident laser power ~ 0.5 mW and back gate voltage  $V_{gs} = 30$  V.

This work in Section 3.4 demonstrated a single TI transistor device for optical chirality detection. By setting the phototransistor in different operating modes with combinations of bias and gate voltages, the circular and linear photoresponses can be switched on or off. The direct measurements of photocurrent that depends on circular polarization only and is spatially uniform will enable chiral photodetectors with a miniature device. The full Stokes parameters are extracted by incorporating the measured linear-polarization sensitive photocurrent on the same device. Therefore, the TI phototransistor shown in this work is an effective way for chirality and polarimetry detection, and can be used in a wide spectrum of applications from polarimetric imaging to quantum information.

#### 3.5 Summary

This chapter discussed the helical photoresponses in Bi<sub>2</sub>Te<sub>2</sub>Se topological surface states studied by electrical transport, i.e., photocurrent measurement in thin-film Bi<sub>2</sub>Te<sub>2</sub>Se devices. Multiple photoelectric effects are identified in the DC condition. The gate and bias voltages are applied to maximize the spin selected TSS contribution to carrier transport. Highly effective helicity control of topological surface states under electrical field gating and the contribution of the helicity controlled TSS to electro-thermal transport are demonstrated under electrical field gating. The biased photocurrent, i.e., the photoconductance serves as an effective optical chirality detector. A comprehensive strategy is also proposed for Stokes parameters analysis that characterizes the elliptical polarization using one single device. On the other hand, the helical-tunability of photo-thermoelectricity and photoconductance provide information in estimating the capability of thermal rectification in TSS using circularly polarized light.

# 4. SWITCHING HEAT TRANSPORT IN TOPOLOGICAL SURFACE STATES

Control of thermal energy transport in topological materials is directly measured and discussed in this chapter. Dynamically tuning of heat transport in solids is scientifically intriguing and engineeringly challenging. Few have been reported due to the dilemmas in the microscale mechanisms of electron and phonon transport. In Bi<sub>2</sub>Te<sub>2</sub>Se thin film, the large contribution from TSS electrons serves as an electrostatic knob of heat transport and hence can be implemented as a thermal transistor. A semiconductor model is built to evaluate the electrostatic gating effect of a suspended thin film during a gate-dependent thermal conductivity measurement. An optical gating method using a dielectric layer with optically tunable built-in charged region is developed to resolve the trade-off between the effectiveness of the electrostatic thermal transistor can be continuously and repetitively switched by ON/OFF ratio ~ 2.8 at room temperature within ~ 10s seconds. Temperature dependence is also studied in seeking the origin of the large Lorenz number. This Chapter is a further step and closely related to Section 2.2, hence some details are not repeated.

#### 4.1 Introduction to Thermal Switches

Thermal switches are devices that turn the heat transfer rate on and off using certain external control knobs. The general definition can include some configurations that e.g., bring parts in and out of contact, pump thermally conductive fluid in and out of the channel, and other subtle configurations with moving parts (Cho et al, 2008; Du et al., 2021; Li et al., 2015) to switch the heat transfer. These can be seen as an analog of a knife-throw switch or mechanical relay among electrical switches. Beyond these, it is always intriguing to implement a solid-state thermal switching solution with no moving parts, fast/real-time switching, and other merits, which can be specifically termed as thermal transistors.

Rapid progress in nanoscale thermal transport research, including studies of heat transfer in nanomaterial and nanostructures and understandings of the microscale energy carrier dynamics,

enabled engineered materials with thermal conductivity tuned beyond nature, e.g., "phonon-glasselectron-metal" for thermoelectrics, (Rowe, 1995) and compliant but thermal-conductive for thermal interfaces, as we introduced in Chapter 1. So far, very few demonstrations were reported for effective thermal transistors. The implementations are all based on either electrical field/temperature-induced phase/structure transition (Ihlefeld et al., 2015; Lee et al., 2017; Oh et al., 2010; Zheng et al., 2011), or electrochemical intercalation (Cho et al., 2014; Kang, Ke, & Hu, 2017; Sood et al., 2018). These works showed the thermal conductivity either tuned by  $\sim 10\%$ , (Ihlefeld et al., 2015) or can be tuned by a few times while the switch is usually on the order of minutes (Sood et al. 2018) or even hours (Cho et al., 2014) since all these methods are tuning the phonon dynamics and require a physical/chemical process to induce certain changes in the lattice structure. On the other hand, switching the electron thermal conduction can be achieved much faster. The electronic carrier density can be electrically gate-tuned by orders of magnitude within time far below 1 second (transistors with sub-nanosecond switching time has been demonstrated for decades). However, the gate-tunable electronic thermal conductivity is also challenging because of the following dilemma. In semiconductors/insulators the electrons only contribute a few percent or less to the total thermal conductivity (compared to phonons). In metals where electronic thermal conductivity dominates, it requires a colossal voltage to deplete the electrons due to the large electron density. It is generally challenging to circumvent this complexity due to the Wiedemann-Franz law that the ratio of thermal and electrical conductivity is within a small range of constant i.e., Lorenz number  $L = 1.5 - 2.2 \times 10^{-8} V^2/K^2$ , while fortunately to be expected in the topological state electrons of Bi<sub>2</sub>Te<sub>2</sub>Se with one of the rare cases of extra-large Lorenz number.

We showed in Section 2.2 that the TSS has a Lorenz number one order of magnitude higher than the Sommerfeld number and dominates the heat conduction in sub-20-nm thin films. It is also shown that the chemical potential can be electrically gated from the Dirac point to the conduction band edge. When gated from Dirac point to conduction band edge, TSS electrons lose dominance and also relax much faster scattering with trivial states. The bipolar diffusion contributes the strongest when the chemical potential is close to the charge neutral point, and reduces when gated to the edge of one band. Thus, either possible mechanisms of the large Lorenz number makes the gate tuned Bi<sub>2</sub>Te<sub>2</sub>Se thin films possible to implement an electrostatic thermal transistor, as shown in the schematic in Figure 4.1, in which the heat conduction channel can be turned on and off when chemical potential accesses the bandgap or the conduction band (TSS or trivial states dominant).



Figure 4.1 Schematics of electrical field-effect thermal transistor based on electrostatic switching of TSS.

## 4.2 Thin Films In-Plane Thermal Conductivity Measurement with Electrostatic Gating

Thermal conductivity vs. carrier concentration is mostly studied by doping or substitution, instead of electrostatic gating. The main reason is that the electrical field-effect would penetrate only 10s of nm into conductive solids due to electrical screening and it is hard to confine heat flow within this thin layer. In Section 3.3 we showed that the electrical field effect in  $Bi_2Te_2Se$  covers the entire thickness of interest, hence, it is possible to study the gate-dependent heat conduction in  $Bi_2Te_2Se$  thin films.

As introduced in Section 1.2, it is preferred to suspend thin films to maintain the sensitivity of thermal conductivity measurement due to the small in-plane thermal conductance of the thin films, and any additional transducer or gating layer will add up the uncertainties.

The first plan is to apply the gate voltage across an air/vacuum gap as shown in Figure 4.2. The SiO<sub>2</sub>/Si substrate is first patterned with circles or strips and etched into holes or trenches. The metal strips are subsequently patterned and deposited between the holes/trenches. Next, Bi<sub>2</sub>Te<sub>2</sub>Se thin films will be transferred onto the substrate and make contact with the metal. The resistance of the Bi<sub>2</sub>Te<sub>2</sub>Se thin films can be used to monitor the field-effect of the electrical gating during the experiment. The thickness of the air/vacuum gap, or the etching depth is a key design parameter. Smaller thickness (of the electrical capacitor) allows a stronger field effect but reduces the resolution of thermal conductivity measurement, since a larger percentage of heat would sink directly through the air/vacuum gap and the temperature distribution depends less on the in-plane heat conduction. Also, the thin film buckling requires a safety clearance (typically ~80 nm) in case

the film fall into contact with the bottom of the trench/hole (measured by AFM). A semiconductor electrostatic model (COMSOL semiconductor module) is used to estimate the field effect, and to find a proper gap thickness for charge-carrier-concentration-dependent study of heat transport based on this trade-off, together with the thermal model introduced in Chapter 2. In practice, we choose silicon wafer with the thickest available 300-nm oxide layer and etch the oxide layer to create the gap (hence the thickness of oxide layer = thickness of the gap, though generally speaking one could etch deeper using deep advanced silicon etching (ASE) procedure) to avoid oxide breaking down.



Figure 4.2 (a) Schematics of micro-Raman measurement of electrically gated thin films. (b, c) AFM histogram of the etched holes with metal contacts.

The model is based on the equilibrium concentration relationships in addition to the electrostatic Poisson's equation  $\rho = e(p - n + N_D^+ - N_A^-) = \nabla \cdot D$ . The electron and hole concentration *n* and *p* are calculated based on the effective density of states of the conduction and valence band  $N_c$  and  $N_v$  (Eq. 4.1). The local Fermi level  $E_{f0}$  is determined from the local electrostatic voltage ( $eV_g = E_{f0}(x) - E_{f0,ground}$ ). The role of doping ( $N_d^+$ ,  $N_a^-$ ) is included in the charge neutrality relationship (Eq. 4.2, is the added charge density  $\Delta \rho$  in quasi-equilibrium, or else the right-hand side equals to zero). COMSOL also provides access to account for secondary phenomenological effects e.g., band narrowing when the parameters are available. Details can be found in COMSOL Semiconductor Module Reference Guide and are not repeated here.

$$n = N_c \exp\left(\frac{q(E_{f_0} - E_c)}{k_B T}\right)$$
(4.1a)

$$p = N_{\nu} \exp\left(\frac{q\left(E_{\nu} - E_{f_0}\right)}{k_B T}\right)$$
(4.1a)

$$\Delta \rho = q(p - n + N_d^+ - N_a^-)$$
(4.2)

$$np = n_i^2 = \sqrt{N_c N_v} \exp\left(\frac{E_{g0}}{2k_B T}\right)$$
(4.3)

Here, the results for thin-film silicon are presented as an example. As showed in Error! **Reference source not found.**(a), three gating conditions and junctions between them are studied. The left and right-side regions are gated across 300-nm silicon dioxide on the bottom surface with and without grounded metal contact on the top. The center is gated across the same thickness of air/vacuum (without grounded contact on the top). For a p-doped ( $N_a = 10^{17} \text{cm}^{-3}$ ) 30-nm thick silicon thin film, the electron concentration at varied gate voltages (calculated till  $V_g = 200$  V, the limit of a typical laboratory voltage source) are mapped in Error! Reference source not found.(bg) and plotted in Figure 4.4. The hole concentration can be calculated from Eq. 4.3, using the effective density of states and the bandgap  $E_{g0}$  (= $E_c - E_v$ ). The charge neutrality or intrinsic carrier concentration  $n_i \approx 10^{9.5} \text{ cm}^{-3}$  for silicon at room temperature. The bottom surfaces of the oxidegated regions start depletion immediately as 1 V positive gate voltage is applied (Error! **Reference source not found.**(b)). The bulk region of the left side is still p-type on average since the top contact is persistently grounded. While that of the vacuum-gated region started much slower and charge-neutrality is reached till  $V_g \sim 15$  V, as shown in Error! Reference source not found.(c), the pattern is similar to a p-i-n junction. Inversion is reached (channel reaches subthreshold and is turning on when a bias voltage is applied) at  $V_g \sim 25$  V and 40 V respectively for oxide-gated and vacuum-gated regions. The vacuum-gated region is fully turned on to  $n \approx 10^{17}$ cm<sup>-3</sup> at V<sub>g</sub> ~ 120 V and finally  $n \approx 10^{19}$  cm<sup>-3</sup> reached at V<sub>g</sub> ~ 200 V.



Figure 4.3 Carrier concentration of thin-film silicon gated across silicon dioxide and vacuum. Charge neutral point  $n, p \sim 10^{9.5}$  cm<sup>-3</sup> (a) Schematic of the gated thin film. (b-g) Log of electron concentration in p-doped silicon when back gate voltage = (b)1 V; (c)15 V; (d)25 V; (e)40 V; (f)120 V; (g)200 V.



Figure 4.4 Carrier concentration in a 30-nm p-type silicon thin film vs. back gate voltage at different regions. Vacuum gap = 300 nm. (a)  $V_g = 0 - 200 \text{ V}$ , (b) zoomed in  $V_g = 0 - 50 \text{ V}$  showing the depletion-inversion process. SiO2 domain/interface denote the average of both left and right side (with and without metal contact).

Per the heat conduction model, when using the 300-nm gap, a vacuum < 100 Pa is needed to maintain a reasonable resolution of the thermal measurement ( $\kappa_{air} \sim 100 \mu$ W/m·K needed for uncertainty increase less than 5%) because of the heat leakage through this thin air gap, which is beyond the capability of the cryostat compatible with our micro-Raman setup (practically possible vacuum level of ~5 kPa, obtained by observing boiling point of water). Based on our heat conduction calculation, a >2-um vacuum gap is needed in rarified air with reduced thermal conductivity hence heat leakage at 5 kPa. A case with a 2-µm vacuum gap is similarly calculated, shown in Figure 4.5, and it is found that, charge neutrality is reached till V<sub>g</sub> ~ 100 V. At V<sub>g</sub> ~ 200 V, electron concentration of the top and bottom surface is  $n \approx 10^{15.5}$  cm<sup>-3</sup> and  $10^{17.5}$  cm<sup>-3</sup> (fully n-type, larger than p-doping concentration) respectively. This thin-film silicon case study gave us an estimation that the proposed micro-Raman technique measurement of gate-dependent thermal conductivity would be practical for thin films below 30 nm and materials bandgap below silicon (~1.1 eV) (despite that the effective density of states also plays a role, not over orders of magnitude as the bandgap does, in Eq. 4.1 and Eq. 4.3).



Figure 4.5 Carrier concentration in a 30-nm p-type silicon thin film vs. back gate voltage at different regions. Vacuum  $gap = 2 \mu m$ .

In addition to the semiconductor electrostatic model for the bulk phase, the role of topological surface states under gating is evaluated as follows. Both TSS and the band-bending induced 2D electron gas are considered to be within 1-nm of the surface. The geometric capacitance during electrostatic charging of the surface states can be neglected since screening is not effective across the small thickness. (The offset capacitance, i.e., the distance of the mean displacement of the wavefunction in a quantum well away from the interface, can be neglected for a similar reason). Hence the electrostatic charging of the surface states is dominated by the quantum capacitance, i.e., the elevated chemical potential required for electrons to fill into the finite density of states.

Similar to the carrier statistics and band structure of graphene (Fang et al., 2007), the quantum capacitance of the topological surface states can be derived as follows. The density of states of 2D electrons with linear dispersion is written as Eq. 4.4. Specific to the TSS, the spin degeneracy  $g_s$  and valley degeneracy  $g_v$  are both 1. By definition, the quantum capacitance  $C_Q$  can be derived as in Eq. 4.5, following Ref. Fang et al., 2007. The quantum capacitance serves as an additional path to the ground contact as introduced in Ref. (Datta, 2004).

$$DOS(E) = \frac{g_s g_v}{2\pi\hbar^2 v_f^2} |E|$$
(4.4)

$$C_Q = \frac{\mathrm{d}(eN)}{\mathrm{d}(\Phi_s)} = -e^2 \int_{-\infty}^{+\infty} \mathrm{d}E \ DOS(E) \frac{\partial f_0(E-E_F)}{\partial E} = \frac{e^2 kT}{2\pi \hbar^2 v_f^2} \ln\left[2\left(1+\cosh\frac{E_F-E_D}{kT}\right)\right] (4.5)$$

In the numerical model in COMSOL, we implement the quantum capacitance as a surface charge density according to the local electrical potential. The surface charge density is calculated using the first-order approximation of the integral of Eq. 4.5, asymptotic to the limit of  $E >> k_B T$ , as given in Eq. 4.6.

$$\rho_{s} = \int_{E_{F,i}}^{E_{F,i}+eV_{g}} C_{Q} dE_{F} = \frac{e^{3}(E_{F}-E_{D})}{4\pi\hbar^{2}v_{f}^{2}kT} \ln\left[2\left(1+\cosh\frac{E_{F}-E_{D}}{kT}\right)\right]$$
(4.6)

Now we add the surface charge density of topological surface states in the semiconductor electrostatic model. The semiconductor band structure properties of Bi<sub>2</sub>Te<sub>2</sub>Se are listed as follows (some are estimated using Bi<sub>2</sub>Te<sub>3</sub> due to the lack of studies of Bi<sub>2</sub>Te<sub>2</sub>Se). The relative permittivity is 113 (Bi<sub>2</sub>Se<sub>3</sub>). The bandgap E<sub>g</sub> = 0.3 eV is obtained from ARPES. The effective density of states of the bulk bands are  $N_c = 3.70 \times 10^{18}$  cm<sup>-3</sup>,  $N_v = 6.57 \times 10^{18}$  cm<sup>-3</sup>, using DOS-based effective mass of Bi<sub>2</sub>Te<sub>3</sub> (m<sub>e</sub>\* = 0.28, m<sub>h</sub>\* = 0.41). (Electron affinity (of Bi<sub>2</sub>Te<sub>3</sub>)  $\chi = 5.3$  eV and the effective mobilities are  $\mu_n = 1200$  cm<sup>2</sup>/Vs,  $\mu_p = 510$  cm<sup>2</sup>/Vs, for polysilicon gate and drift-diffusion of charge distribution in semiconductors) With a  $10^{18}$  cm<sup>-3</sup> doping density of both types, the electron densities under varied back voltages across 300-nm SiO<sub>2</sub> and vacuum are plotted in Figure 4.6.



Figure 4.6 Electron concentration of 15-nm Bi<sub>2</sub>Te<sub>2</sub>Se at different region vs. back gate voltages.  $n_i = 1.54 \times 10^{16} \text{ cm}^{-3}$  (a) n-type doping N<sub>D</sub> =  $10^{17} \text{ cm}^{-3}$ , (b) p-type doping N<sub>A</sub> =  $10^{17} \text{ cm}^{-3}$ .

The gating across the vacuum gap is less effective when taking the screening effect of TSS into consideration. Particularly, the top surface carrier concentration marginally crosses the charge neutral point ( $n_i \sim 1.54 \times 10^{16}$  cm<sup>-3</sup>), which is not sufficient to make an effective electrostatic thermal transistor since TSS on both sides need to be switched for full functionality.

A more effective optical gating strategy is adapted from Ref. (Yeats et al., 2015). Yeats et al. argued they used the impurity traps in the  $SrTiO_3$  substrate that the TI was grown on, though the detailed mechanism is not explained. Instead, Si<sub>3</sub>N<sub>4</sub>, which can be deposited by sputtering using Birck facility, is chosen per its band alignment, as shown in Error! Reference source not found.(a) (Robertson, 2000), and the reason is explained below. In fact, the optical gating can be simply enabled by the semiconductor heterostructures, even without impurities. Photons of a certain wavelength (e.g., x eV) can excite electrons from the (occupied) valence band edge of Si<sub>3</sub>N<sub>4</sub> to the unoccupied conduction band of Bi<sub>2</sub>Te<sub>2</sub>Se, building up the charged layer and a build-in potential in both materials at the interface. The charged layers would persist, as long as both Si<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>Te<sub>2</sub>Se's inner bands present a gap x eV below the valence band edge of Si<sub>3</sub>N<sub>4</sub>, so that the electron vacancies at the valence band edge of Si<sub>3</sub>N<sub>4</sub> cannot be refilled by photons with that energy. Excitation from Bi<sub>2</sub>Te<sub>2</sub>Se to the unoccupied conduction band of Si<sub>3</sub>N<sub>4</sub> may also work but not as persisting since the electrons are able to find their way to relax back with the assistance of impurities. Hence, the candidate dielectrics are preferred to have 1) a valence band lower than the valence band edge of Bi<sub>2</sub>Te<sub>2</sub>Se by an amount smaller than the photon energy used for optical switching; 2) a bandgap covering the bandgap of  $Bi_2Te_2Se_1$ , i.e., the conduction band edge in the dielectrics is higher than the conduction band of Bi<sub>2</sub>Te<sub>2</sub>Se. The second condition is required for the dielectric to be an insulator for both electrons and holes for Bi<sub>2</sub>Te<sub>2</sub>Se. For example, when silicon is used as the channel material, SrTiO<sub>3</sub> substrate whose conduction band edge is ~0.1 eV below that of silicon, is not a good choice for building up charges because the (conduction band) electrons can freely move between silicon and SrTiO<sub>3</sub>. Impurities provide other possibilities and may enable large bandgap dielectric such as SiO<sub>2</sub> whose band edges are far beyond excitation access of available photon energies, but are not necessarily required for optical gating to work.



Figure 4.7 (a) Electronic band alignments of candidate dielectrics; (b) Schematics of Bi<sub>2</sub>Te<sub>2</sub>Se (BTS) band structure with chemical potential tuning using optical illumination.

As explained above, due to lack of knowledge of the inner-shell band structure and energy level of impurity states, it is more practical to obtain the optical gating effect empirically using two light sources with distinctive photon energies on the order of a few eVs, e.g., 2 eV and 3 eV to achieve excitation between different energy levels. LEDs, which as a broadened spectrum are preferred hence precise matching of the (unknown) energy levels is not required. To check the effectiveness of optical gating in sputtered Si<sub>3</sub>N<sub>4</sub>, thin-film Bi<sub>2</sub>Te<sub>2</sub>Se transistors are fabricated on SiO<sub>2</sub>/Si, similar to those in Section 3.3. A 3-nm Si<sub>3</sub>N<sub>4</sub> layer is then coated on the top of the devices. The dark current is measured after red/UV light exposure (Thorlabs LED385L and LED630L, focus to spots ~0.5 mm). The sheet resistance can hence be extracted and compared with the transfer curve  $(I_d - V_g)$  measured under pure electrical gating as shown in Figure 4.8. The measurement is performed at a low temperature of -148 C for the clear ON/OFF. It can be observed that device can be turned off by the red light and on by the UV light. One possible explanation is that the  $Si_3N_4$  valence band edge can be efficiently depopulated by the UV light, leaving positive charges to gate Bi<sub>2</sub>Te<sub>2</sub>Se chemical potential toward conduction band (Figure 4.7(b)) and turning on the charge-transport channel. In the inverse process, these vacancies in Si<sub>3</sub>N<sub>4</sub> valence band edge can be filled by red light excitation from the inner band ~1.9 eV below, neutralizing the heterostructure and moving the chemical potential of Bi<sub>2</sub>Te<sub>2</sub>Se toward Dirac point/valence band, hence, turning off the device. The two transition processes at the heterojunction allow the optical gating that switch between ON and OFF states as a substitute of the electrical gating. Of course, de/activation of some certain impurity levels within the bandgap can lead to the same effect. The optical gating is effective to tune the chemical potential to the OFF state comparable to electrical gating accessing the TSS, and to a certain level of ON state which is close to the conduction band edge (recall Section 3.3 and 3.4). Notice that the time span here is due to the excitation of the trap states, rather than response time of the Bi<sub>2</sub>Te<sub>2</sub>Se to electrostatic gating. The intrinsic switching time, limited by the Bi<sub>2</sub>Te<sub>2</sub>Se material, should be on the order of ~ 1 ns or lower (some work showed to be even faster by THz experiments (e.g., Seifert et al., 2017).



Figure 4.8 Sheet conductance of a 16- nm Bi<sub>2</sub>Te<sub>2</sub>Se transistor with Si<sub>3</sub>N<sub>4</sub> coating under UV/red light illumination, compared with pure electrical gating, measured at -148 C.

Now, the gate-dependent thermal conductivity measurement technique is established as shown in Figure 4.9. Thin-film Bi<sub>2</sub>Te<sub>2</sub>Se sample is first transferred and suspended on holey SiN films (Ted Pella 21536-10, recently available 5- $\mu$ m holes compared to the 2.5- $\mu$ m used in Section 2.2 for better resolution) using PVA/PMMA method, similar to Section 2.2. Then, 3-nm Si<sub>3</sub>N<sub>4</sub> is sputtered on the backside of the Bi<sub>2</sub>Te<sub>2</sub>Se, flipped bonded using photoresist on a silicon wafer. The deposition rate is set at ~0.8 nm/min (90 V AC driven plasma), in an inert argon environment. The shutter is open/closed intermittently (20 sec / 2 min) to avoid overheating of the samples. After sputtering, the samples are submerged in Remover PG (NMP solution) to remove the bonding photoresist. A tiny amount of MgSO<sub>2</sub> is dissolved in Remover PG (solubility is very low, exact

concentration is not measured) to discharge since there is no metal contact for grounding. During micro-Raman measurement, the red/UV light is incident on the backside (the same side as sputtered Si<sub>3</sub>N<sub>4</sub>). Micro-Raman thermometry is performed similarly as introduced in Section 2.2, in a nitrogen environment at atmospheric pressure. Since the thermal conductivity of sputtered Si<sub>3</sub>N<sub>4</sub> thin film cannot be measured to a high accuracy, it is assumed to be 3 W/m·K in all following calculations. Since the Raman technique measures the overall in-plane thermal conductance of Bi<sub>2</sub>Te<sub>2</sub>Se and Si<sub>3</sub>N<sub>4</sub> in parallel, an overestimation of  $\kappa_{SiN}$  leads to a negative systematic error of  $\kappa_{BTS}$ , and vice versa, which can be quantified using the heat conduction model. This systematic uncertainty applies a bias to all results and does not affect the main conclusion hence is not included in the propagation analysis. Despite the deposit Si<sub>3</sub>N<sub>4</sub> makes an additional conduction channel that reduce the sensitivity of thermal conductivity measurement, the uncertainty is still acceptable due to the improvement using larger holes for thin film suspension and will be indicated below by the error bars.



Figure 4.9 Schematics of the optical gated thermal conductivity measurement of Bi<sub>2</sub>Te<sub>2</sub>Se thin films using micro-Raman thermometry.

## 4.3 Realization of Electrostatic Thermal Transistors

 $Bi_2Te_2Se$  thin films with  $Si_3N_4$  gating media is prepared using the procedure described in Section 4.2. To take advantage of the TSS contribution and show the large ON/OFF ratio of the

thermal transistor, we focused on the films below 20 nm, and measured two other thicker samples for reference. Figure 4.10(a) summarized all the measured Bi<sub>2</sub>Te<sub>2</sub>Se thermal transistors fabricated in two batches. Three of the samples (9 nm, 13 nm, and 14 nm) successfully demonstrate switching of thermal conductivity upon the red and UV light illumination. All these three samples were standing-alone on different substrates so not affected by red/UV illumination cycles of the others (testing procedure and cycles will be explained below). The ON and OFF state thermal conductivities shown here are from the long illumination cycles with the largest ON/OFF ratio. A large thermal ON/OFF ratio as high as 2.8 is observed on the 9-nm sample. The ON/OFF ratio of the other two thermal transistors with slightly larger thicknesses are also greater than 1. The 56 nm film showed a slight variation of thermal conductivity on the margin of the metrology's resolution upon optical gating; hence the results are color-marked but not analyzed in detail. The results were plotted with the bilayer transport model proposed in Section 2.2, which makes a good prediction of the thermal conductivity. This indicates we are indeed tuning the TSS contribution to thermal conductivity, further confirms and enhances the previous argument in Section 2.2 that the large thin-film thermal conductivity and large Lorenz number are originated from TSS electrons, and also infers that the  $\kappa_{Si_3N_4} = 3 \text{ W/m} \cdot \text{K}$  is a reasonable assumption. The "dead" samples that do not respond to the optical gating (within the metrology resolution) are also plotted. Thermal conductivity of all dead samples are close to that of the OFF states of thermal transistors, the thickfilm reference values, and the prediction of trivial cases. Their TSS may be impaired during sputtering, or the illumination cycles when they are on the same substrate with another sample. There is also a small chance that it is exfoliated from the oxidized surface of the bulk material. These values together suggest the thermal conductivity contributed from phonons and bulk state electrons.

Two types of ON/OFF cycling tests are performed for the optically gated thermal conductivity measurement. Figure 4.10(b, c) presents the power (of Raman laser incidence) dependent Raman results taking the 9-nm film for example. One, called long illumination, is to place the sample directly on top of the LEDs (without external focusing, backside facing LEDs) for from 5 hours to overnight, ensuring the Si<sub>3</sub>N<sub>4</sub> gating media is fully exposed, and the charge sites are saturated. Here we take advantage that the chemical potential of Bi<sub>2</sub>Te<sub>2</sub>Se thin films tend to move towards the conduction band (while the TSS still exists) so that negative gating (by optical means) beyond the charge neutral point and inverting to the valence band is hard (need special

precaution as in Section 3.4), hence there is less a concern for long red illumination to turn off the heat transport again by reaching the valence band. After long illumination, micro-Raman measurements with ~10 incident power points are conducted as shown in Figure 4.10(b, c) with solid dots and linear fitting, same as in Section 2.2. The long illumination results and the subsequent Raman tests provide the resolution of thermal conductivity measurement that showed in Figure 4.10(a), and sketch the thermal ON/OFF states of a thermal transistor.



Figure 4.10 Optically gated Bi<sub>2</sub>Te<sub>2</sub>Se thermal transistor characteristics at room temperature. (a) Thickness-dependent thermal conductivity at the ON/OFF states of BTS thin-films. TSS thermal conductivity models are taken from Ref.(Luo et al., 2018). A few dead BTS films in the same batch with the 9-nm are also plotted. (b, c) Raman shift-power relation of the 9-nm film under red and UV illumination. Solid dots and their linear fitting lines are the results from Raman measurements at 9 different power levels after long illumination; diamonds are from 3 different power levels after each train of pulsed illumination with controlled exposure dosage. (d) Time history of thermal conductivity under red and UV illumination.

The other type of the cycling test is using pulsed illumination, enabled by a LabVIEW code giving a certain number of 1-sec-long pulses of voltage with a duty cycle of 0.1 (1 sec on, 9 sec off) to drive the LEDs. The illumination time (in seconds) in Figure 4.10(b-d) is total number of pulses that the samples receive. The rise time of the LEDs are far below 1 sec. The current is monitored during a large number of pulses and does not show a significant drift, indicating there is no temperature build-up. Hence, each pulse should provide the same fluence for either long or short pulse trains, and the dose of the optical gating is precisely controlled. A reduced scale Raman measurement is performed between the pulse trains (after a certain time of illumination) with only three different power incidences, in order to obtain the experimental results within a short time. The Raman data for red and UV pulse illumination are also plotted in Figure 4.10(b, c) using hollow diamonds, marked by red and violet arrows, respectively, to indicate the beginning and final states. The pulse illumination results illustrate the continuous process of optical gating/switching on or off the thermal transistor, and can be further used to sketch out the thermal conductivity evolution with optical gating. The thermal conductivity of each time step is similarly extracted using the same procedure as above (with lower resolution) and visualized in Figure 4.10(d). There are a few/teen seconds of basin/plateau before the thermal transistor is switched for both red and UV illumination. In principle, optical excitation at the beginning should be the most effective because all the states are unexcited (per this certain type of excitation), and then become less effective as more states are excited, forming an exponential curve. This is to say there is a comparatively wide range of chemical potentials within the bulk bandgap for the TSS to exhibit the large to thermal conductivity. Within this range, the TSS behavior is less sensitive to the exact chemical potential. We define the time lapse for the thermal transistor to switch from 20% to 80% (due to the low resolution here) as the switching time. The ON and OFF switching time for the 9nm film are 15 sec and 40 sec, respectively. The ratio is not very close to the photon flux of the illumination, which may be due to the existence of traps states at multiple energy levels.

To demonstrate that the thermal transistor can be repetitively switched on and off, all the thermal conductivity results of the 9-nm thermal transistor at room temperature after red/UV illumination cycling are summarized in Figure 4.11. The device first experienced long illuminations to obtain the ON/OFF thermal conductivity presented in Figure 4.10(a), also as the solid dots in Figure 4.10(b, c). Then, pulse trains (with a coarser length of time steps) of red and UV light are applied and Raman measurement is performed after each time step. This cycle is also

used to estimate the switching times and the time-step resolution needed to resolve them. Then, fine time-stepped pulse trains are used to obtain the results shown in Figure 4.10(b, c) (open diamonds) and Figure 4.10(d). A series of low-temperature tests are performed afterward and will be discussed below. After the low-temperature measurements, two more long illumination cycles are performed to further verify the repeatability of switching. It is found that the thermal transistor is able to preserve functionality after all these (5 room-temperature + 2 low-temperature) cycles, despite the slight reduction of ON/OFF ratio after low temperature measurements, which may be due to some condensation affecting the surface. Finally, we heat the thermal transistor to 200°C for 60 min, which is known to kill the TSS due to the Se/Te immigration (Bahramy et al., 2012, Tian et al., 2015). The thermal conductivity of the killed thermal transistor is measured to be 0.95 W/m·K, close to other dead samples. This gives another evidence that the extra thermal conductivity is originated from the TSS.



Figure 4.11 ON/OFF cycling of the 9-nm thermal transistor. (a) First cycle under long illumination; (b-e) second and third cycle under pulsed illumination; (f) two more cycles under long illumination. Two cycles performed under low temperature between (e) and (f) are not showed in this figure. The hour-long illuminations are using unfocused LED, and the second-resolved are using focused LED. Thermal transistor finally killed heated to 200°C for 60 min (black triangle).

We further performed the optical gate-dependent thermal conductivity tests at varied lower temperatures using a liquid nitrogen cryostat. A few additional efforts beyond the procedure in Section 2.2 are needed. A long working-distance objective is used to accommodate the distance between the sample and the front side window. The optical absorption at low temperatures is measured separately at each bath temperature for each film. The transmitted power through the suspended thin film and through the hole next to (10  $\mu$ m apart from) it are measured when the sample is place on the cryostat, assuming a 10- $\mu$ m displacement does not affect the millimeter-level aperture stop of the hole of the heating/cooling block. Also notice that the temperature we report is based on the bath temperature, while the results in fact mean the average temperature from the bath temperature to 50-80 °C above achieved during typical Raman measurements.

The temperature dependence of ON/OFF thermal conductivity of the most representative 9-nm thermal transistor is shown in Figure 4.12. Interestingly, the ON state (total, TSS, phonon, and bulk electron) thermal conductivity did not change much with temperature, while the OFF state (phonon and bulk electron) thermal conductivity reduced slightly, though marginally within the uncertainty level. The thermal transistor can operate in a quite wide range, from liquid nitrogen temperature to ~90 °C, which is approaching its degrading temperature (TSS Bi<sub>2</sub>Te<sub>2</sub>Se does not survive >~110 °C for a long time). The TSS contribution, by subtracting the ON and OFF state, is also plotted. It can be concluded from the temperature dependence that the large TSS thermal transport (large Lorenz number) cannot be solely due to bipolar diffusion. As introduced in Section 2.2.2 and Eq. 2.8, the microscale picture of bipolar diffusion is thermal energy carried by thermally excited electron-hole pairs near the CNP. The extra-large thermal conductivity of TSS should reduce sharply with temperature if it is due to bipolar diffusion, which is not observed. On the other hand, a counterplaying contribution of hydrodynamic interaction of electrons, which may increase with temperature decrease, (Crossno et al., 2016) may still coexist with the bipolar diffusion. It also needs to be pointed out that the reduced OFF state (phonon + bulk electron) thermal conductivity cannot be explained by bipolar diffusion of the bulk states, because the OFF states are achieved by gating the chemical potential away from the CNP towards the conduction band edge, where electron-hole pairs are much less likely to be formed by thermally excited.



Figure 4.12 Temperature dependent thermal conductivity switching of the 9-nm thermal transistor.

#### 4.4 Summary

This chapter demonstrated the gate-dependent thermal conductivity measurement of thinfilm Bi<sub>2</sub>Te<sub>2</sub>Se. A gate-dependent thermal conductivity measurement technique for thin films based on micro-Raman thermometry and electrostatic gating across vacuum was proposed. An associated numerical tool was developed to design the samples, obtain the optimized experimental parameters, and evaluate the limitation of this method. Furthermore, an optical gating method was developed, when vacuum gating is not effective with the available equipment. Gate-dependent thermal conductivity of Bi2Te2Se was measured and electrostatic thermal transistors were thus demonstrated. The thermal conductivity can be switched continuously by an ON/OFF ratio of 2.8 at room temperature within tens of seconds, and the thermal transistor can operate in a wide temperature range from liquid nitrogen temperature to its degradation temperature. The switching time can possibly be improved to nanoseconds when using directly electrical gating. Good repeatability over multiple ON/OFF cycles was also shown. The temperature dependence study also improved understanding of the origin of the large TSS thermal conductivity and large Lorenz number. The reported electrostatic thermal transistor with a large ON/OFF ratio and fast switching potentials would imply the possibilities of smart thermal devices such as heat routers for active thermal management and pyroelectric devices that harvest energy from steady-state heat source with higher efficiency.

## 5. SUMMARY AND FUTURE WORK

## 5.1 Summaries and Conclusions

The energy carrier transport in topological materials is investigated using combined optothermal and optoelectronic methods.

In Chapter 2, the in-plane thermal conductivities of thin-film topological materials were studied using micro-Raman thermometry. An unexpected large thermal conductivity up to ~4 W/m·K in topological insulator Bi<sub>2</sub>Te<sub>2</sub>Se was found in very thin films. The thickness-dependent tests attributed the large thermal conductivity to the surface contribution. With the help of electrical and magneto transport measurements, an extraordinary large Lorenz number of more than 10 times of the Sommerfeld value was found in the TSS. Breaking of the Wiedemann-Franz law in TSS in Bi<sub>2</sub>Te<sub>2</sub>Se thin films pointed to unique carrier dynamics, which along with the large electronic thermal conductivity of TSS opened an opportunity for controlling heat transfer through electrical field-effect and/or spin injection. The micro-Raman optothermal method was also used to measure the Weyl semiconductor tellurium thin film with van der Waals stacking of spiral chains structure. Deep-etched trench grid substrates were fabricated, and a capillary-force assisted transfer method was adopted to prepare the suspended solution-grown tellurium thin films for thermal conductivity measurement. Anisotropy no less than 1.3 of in-plane thermal conductivity was observed along and across the atomic chain. Time-domain thermal reflectance helped to study the out-of-plane transfer, and first-principles modeling unraveled the origins of high three-dimensional anisotropy as the anisotropic phonon dispersion and the difference in interface suppression.

Photocurrent study in Chapter 3 showed the TSS electron transport characteristics under optical spin injection. The different incident wavelengths and gate/bias voltage were applied to excite and modulate the TSS. The results showed that the TSS electrons are the dominant carriers in electrical transport and are expected also to be the dominant energy carriers in thermal transport. The photo-thermoelectricity and photoconductance under circularly polarized light incidence provide information to estimate the helical-tunability of TSS electronic heat transfer. The maximum helical modulation in each case was also estimated. In addition, the investigation also nurtured fruits beyond the originally conceived ideas. Deep tuning of photo-thermoelectricity by 5 times was observed upon changing the polarization of the incident light. The gate tunability of photo-thermoelectricity is also broadened using circularly polarized light comparing to the unpolarized results. The helicity-dependent photoconductance was also discovered to be a competitive candidate for optical chirality detection, and single-device Stokes parameters analyses were implemented using a Bi<sub>2</sub>Te<sub>2</sub>Se phototransistor. The photoconductance was found tunable as either solely helicity-dependent or polarization-independent under different gate voltages, i.e., the chirality detection mode, and intensity detection mode respectively. Detection of the linear polarization direction was also implemented using the linear photogalvanic current of the same device. The polarimetric phototransistors were demonstrated having a comparable chirality sensitivity to the state-of-the-art metamaterial-based solutions.

A thermal transistor based on the highly thermal conductive topological surface state electron was presented in Chapter 4. A gate-dependent thermal conductivity measurement technique using micro-Raman thermometry and electrical gating across air/vacuum gap was proposed, and a numerical model was developed to evaluate the electrical field effect and tuning capability. An optical gating method using a thin  $Si_3N_4$  layer deposit on suspended thin film samples-under-test was further developed and proven valid for deeper electrostatic control. The optical gating method was applied to study the gate-dependent thermal conductivity of topological insulator thin films. Dynamic tunability of the overall thermal conductivity was found in  $Bi_2Te_2Se$  thin films, when the large thermal conductance of the topological states was controlled by the optical gating. Electrostatic thermal transistors were hence implemented with large ON/OFF ratio and fast switching time. The temperature-dependent study of thermal conductivity under gating also provided better understanding of the large contribution to heat transport (large Lorenz number) in the topological state.

#### 5.2 Future Works

Despite the success of realization of electrostatic thermal transistor in Chapter 4, the optical gating method is not as convenient, and more challenging to scale up, compared to conventional metal-oxide-semiconductor structure. Also, the understanding of TSS electrons contribution is not comprehensive since the micro-Raman method was measuring the overall thermal conductivity (though extracted using the bilayer model).

The main challenge of implementing metal-oxide-semiconductor structure is the loss of resolution due to the additional heat conduction channel. In steady-state measurement, including

the well-accepted electrothermal micro-bridge device, the thermal resistor network is static and only associate to geometries and thermal properties, which do not have many choices of design. While transient thermal metrology including time/frequency domain techniques are capable of e.g., confining thermal penetration depth, canceling absolute heating power, etc., and empowered more flexible thermal measurements and eliminate certain sources of uncertainties. Specifically, transient Raman thermometry using varied is reported to be able to measure in-plane thermal conductivity for supported thin films.(Li et al., 2017; Xu et al., 2020) Hence, electrostatic thermal transistors controlled by actual electrical voltage could be demonstrated using transient Raman technique. Then, one could perform thermal measurements using the same samples for electronic and magneto transport studies, which provide more quantitative and in-depth understanding of topological electron behaviors.

Electronic thermal conductivity in solids is generally not possible to be measured separately from the phonon, due to their strong coupling. In steady-state, it is doable only in some particular case e.g., when only electrons associate with the surface in topological insulators (Luo et al., 2018) (surface phonons, even when exists, only contribute to scattering but not transport) or non-coupled electrons and phonons in low-temperature graphene (Crossno et al., 2016). While in the time-domain, hot electron dynamics can be analyzed before/during its coupling with sub-picosecond resolution (Qiu & Tien, 1993) and the transport properties can be studied when the pump-probe system is equipped with spatiotemporal mapping (Block et al., 2019; Segovia & Xu, 2021). An ultrafast spatiotemporal measurement of gate-dependent electronic thermal conductivity would be a great progress in understanding the exceptional thermal properties of topological surface states.

Thermal rectification, or thermal diodes, is another intriguing topic in thermal management application and heat transfer physics.(Liu, Wang, & Zhang, 2019) The direction-dependent thermal conductivity in the same axis was first observed back in 1936 (Starr, 1936) but scarcely reported in later years using non-mirror-symmetric structure in macroscale or atomic scales (Chang et al., 2006; Li, Wang, & Casati, 2004; Li et al., 2012; Liu et al., 2019; Roberts & Walker, 2011; Wang et al., 2014; Wehmeyer et al., 2017). The nonreciprocal TSS transport along with its large contribution to thermal conduction may open unprecedented path for thermal rectification with real-time tunability. With the knowledge obtained from thermal conductivity and helical

photocurrent measurements, the controlled TSS transport of charge and thermal energy can be understood in the following (Onsager's reciprocal) framework schemed in Figure 5.1.



Figure 5.1 Analytical framework for thermal rectification based on helicity-controlled TSS transport.

Electrons as a carrier can be driven by both electrical and thermal motive forces, and the measurable effects include both charge and heat flow. The first rectification effect is based on the helical modulation of TSS conductivity. The helicity-dependent photoconductance presented in Section 3.4 can be modulated by ~2.5% compared to the DC conductance. The spin selected TSS electrons are also expected to contribute to electronic thermal transport nonreciprocally. Since the circular photoconductivity is originated from TSS electrons, which showed to have a large Lorenz number, the thermal conductivity using the micro-Raman method is challenging since a 100+°C temperature difference is required for sufficient fidelity. While the microdevice method may be sufficient to perform the measurement (Kim et al., 2001; Sadat et al., 2012, 2013; Zheng et al., 2013). On the other hand, the helical photocurrent also carriers heat due to the Peltier effect, where the Peltier coefficient can be obtained from the Seebeck coefficient using Onsager reciprocal relation (Section 1.1.4). The helicity controlled thermal energy transfer is estimated by the

tunability of thermoelectric properties. Despite the phenomenological similarity, the incident circular polarization in this mechanism is the driving force of the rectified heat flow, and the device is more a microscale solid-state analog of heat pumps. Under the aforementioned experimental condition, the Peltier heating and cooling at the contacts generated by the circular photogalvanic current are calculated by the numerical model on top of the laser heating. The same numerical framework including laser heating, thermoelectrics, and heat transfer processes is again used to predict the Peltier heat flow. The optical heating, parametrized by the measured laser power and beam size, and the optical absorption derived from the dielectric constants, served as a volumetric heat source in the heat conduction model. Besides the optothermal heating, the Peltier heat flow and Joule heating are calculated using the helical photocurrent measured in the experiment. The temperature distribution is then calculated using the volumetric heat source consists of laser heating, Joule heating, and Peltier effect. The difference between the average temperatures at the contacts represents the helical Peltier effect.

Here, an estimation is presented as a guideline of the required metrology. Specific to the 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device discussed in Section 3.3 and its photoresponsivity, the temperature difference at the contacts is calculated to be 0.019 K under -30V back gating (the measurability is  $\sim 2\%$ ). We also estimated the Peltier heating/cooling if the Bi<sub>2</sub>Te<sub>2</sub>Se device channel were suspended in the air with minimized substrate shunting of the heat flow ( $\Delta T \sim 2.5$ K). The temperature contrast on the two electrodes is plotted in Figure 4.4b. The helicity-controlled heat flow results in a measurable temperature difference across itself, though challenging to distinguish using the micro-Raman thermometry (~1 K resolution for Bi<sub>2</sub>Te<sub>2</sub>Se (Luo et al., 2018)), can be easily measured by micro-thermistors (Sadat et al., 2012, 2013; Zheng et al., 2013). Additionally, it needs to be pointed out that the strong laser heating is the key challenge to demonstrate this rectification. To show the contribution of the Peltier contribution of the helical photocurrent compared to the Joule heating and laser heating, the measurability of temperature difference due to the Peltier effect is defined as the ratio of the temperature difference at the two contact and that of the entire device,  $M = |T_{c1} - T_{c2}|/(T_{max} - T_{min})$ . The measurability is calculated assuming the device has different Seebeck coefficients and circular photo-response, and the two-parameter mapping is shown in Figure 5.2(a). The few percent measurability indicates that the temperature distribution is a single peak due to the dominance of the laser heating, and the rectification is the asymmetry of this peak. The accuracy of the thermal rectification measurements will be vulnerable to any

motion of the test stage, and also affected by the device asymmetry (imperfection from fabrication). A differential measurement of the thermistors' resistance that locks-in to the periodic varying chirality of circularly polarized light (e.g., rotation of QWP) is required to perform successful measurements.



Figure 5.2 Thermal rectification due to Peltier effect of helical photocurrent. (a) Measurability of helical Peltier temperature difference vs. the Seebeck coefficient and the photocurrent, under 1 mW incident power on the 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device. (b) Temperature difference at the contacts of supported and suspended 11-nm Bi<sub>2</sub>Te<sub>2</sub>Se device calculated based on the measured helical photocurrent in Section 3.3.

To summarize the perspectives of future research, advanced metrology especially temporal techniques e.g., transient Raman thermometry and spatiotemporal pump-probe can be applied to further study the thermal energy transport in topological states. Based-on the knowledge of heat transport and TSS concentration control, varied types of rarely-precedent thermal devices, though challenging, can also be realized.

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