OPTOELECTRONIC STUDY OF TOPOLOGICAL INSULATORS
AND TOPOLOGICAL INSULATOR-MAGNETIC INSULATOR
HETEROSTRUCTURES

A Dissertation in
Physics
by
Yu Pan

© 2017 Yu Pan

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2017
The dissertation of Yu Pan was reviewed and approved* by the following:

Nitin Samarth  
Professor of Physics  
George A. and Margaret M. Downsbrough Department Head  
Chair of the Committee  
Dissertation Advisor

Chaoxing Liu  
Assistant Professor of Physics

Jun Zhu  
Associate Professor of Physics

Venkatraman Gopalan  
Professor of Materials Science and Engineering

*Signatures are on file in the Graduate School.
Abstract

Topological insulators have attracted much contemporary interest due to the gapless spin-textured surface states which reside within the bulk band gap. The spin-momentum locking in these helical surface states provides a unique opportunity for "topological spintronics" devices that function at technologically relevant temperatures (300 K and above). Optoelectronic methods have been adopted to control electron spin and charge currents in 3D TIs. In particular, experiments have shown that circularly polarized light induces a directional helicity-dependent photocurrent (HDPC) in 3D TIs. The ready observation of this phenomenon at 300 K promises interesting opportunities for developing opto-spintronic devices wherein electron currents might be steered optically. Progress toward such technological applications is however impeded by a lack of understanding about the physics underlying this phenomenon. Thus, a comprehensive study of the helicity-dependent photocurrent in 3D TIs as a function of the incidence angle of the optical excitation, its wavelength and the gate-tuned chemical potential is described in the first part of the dissertation (Chapter 3). I unambiguously identify the circular photo-galvanic effect as the dominant mechanism for the helicity-dependent photocurrent. Additionally, a theoretical analysis and numerical calculation of the photocurrent relates the directional nature of the photocurrent to asymmetric optical transitions between the topological surface states and bulk bands.

Though the topologically protected surface states are interesting by its own, the emerging field of 'topological spintronics' relies on interfacing the helical Dirac surface states of TIs with magnetism. Heterostructures that combine TIs with magnetic insulators (MIs) are particularly relevant within this context. The magnetic proximity effect and the spin pumping at the interface are of great importance in the research field of topological spintronics. Thus, the second topic of the dissertation (Chapter 4) is to explore the spin pumping by light illumination on the heterostructure. The discovery of a spin-dependent photocurrent (PC) is a signature of the spin pumping, which maps out the magnetization at the interface, as confirmed by a direct comparison with magneto-optical Kerr effect measurements. Further insight into this phenomenon is gained by studying the spin-dependent PC
as a function of the chemical potential of the TI film, as well as by examining its variation with the temperature and the wavelength of the optical excitation. The optoelectronic study in the heterostructure of TI-MI not only identifies the spin pumping, but also provides a new method for magnetization measurements.
# Table of Contents

List of Figures ix  
List of Tables xviii  
List of Symbols xix  
List of Acronyms xx  
Acknowledgments xxii  

Chapter 1  

Introduction  
1.1 Topology in condensed matter 1  
1.1.1 What is topology? 1  
1.1.2 Topological invariant for gapped band structures 2  
1.1.3 Bulk-boundary correspondence and the edge states 3  
1.2 Topological insulators 4  
1.2.1 2D topological insulator 5  
1.2.1.1 HgTe/CdTe quantum well 5  
1.2.2 3D topological insulator 7  
1.2.2.1 Bi$_2$Se$_3$ family 9  
1.2.2.2 Exotic physics of the Dirac surface states 10  
1.3 Topological insulator- magnetic insulator heterostructures 12  
1.3.1 Topological spintronics 13  
1.3.1.1 Spin-orbit transfer torque 13  
1.3.1.2 The birth of topological spintronics 14  
1.3.2 Interfacing topological insulators with magnetic insulators 15  
1.3.2.1 Magnetic proximity effect at the interface of TI and MI 16  
1.3.2.2 Spin pumping at the interface of TI-MI 17  
1.4 Photo-galvanic effect 18
1.5 Outline ................................................................. 19

Chapter 2

Experimental Methods .................................................. 21

2.1 Device fabrication .................................................... 21
   2.1.1 Sample growth by molecular beam epitaxy ............... 21
   2.1.2 Photo-lithography and etching ............................. 23
   2.1.3 Fabrication of the top gate ................................. 25
      2.1.3.1 Lift-off of the gate material ......................... 29
2.2 Tuning the chemical potential with gating ...................... 30
   2.2.1 Electro-static gating with field effect transistors ........ 30
   2.2.2 Persistent optical gating ................................ 31
2.3 Low-noise photocurrent measurement .......................... 32
2.4 Magneto-optical Kerr microscopy ............................... 34

Chapter 3

Helicity Dependent Photocurrent in Topological Insulators ...... 37

3.1 Introduction ........................................................ 37
3.2 Polarization dependent photocurrent measurements ............ 38
   3.2.1 Experimental set-up .................................. 38
   3.2.2 Extraction of the helicity dependent photocurrent ...... 39
   3.2.3 Physical mechanism of the helicity dependent photocurrent . 40
   3.2.4 The directionality of the helicity dependent photocurrent .. 43
3.3 Study of the helicity dependent photocurrent with a top gate . 45
   3.3.1 Transport properties of the (Bi\textsubscript{1-x}Sb\textsubscript{x})\textsubscript{2}Te\textsubscript{3} thin film ......... 45
   3.3.2 Gate voltage dependence of the helicity dependent photocurrent 46
   3.3.3 Wavelength dependence of the helicity dependent photocurrent 48
   3.3.4 Photocurrent from the bottom surface illumination ........ 49
3.4 Theoretical analysis of the helicity dependent photocurrent .... 50
   3.4.1 First principles calculation of the band structure of (Bi\textsubscript{0.5}Sb\textsubscript{0.5})\textsubscript{2}Te\textsubscript{3} .... 51
   3.4.2 Optical transitions between the surface states and the bulk states ................................................. 52
3.5 Understanding of the experimental helicity dependent photocurrent with theoretical analysis ......... 54
   3.5.1 Numerical calculation of the photocurrent ............... 54
   3.5.2 Schematic picture of helicity dependent photocurrent reaching maximum at the Dirac point .............. 56
   3.5.3 Understanding of the asymmetric helicity dependent photocurrent around the Dirac point .......... 56
3.5.4 Understanding of the wavelength dependence of the helicity dependent photocurrent ........................................ 58
3.5.5 Contributions to helicity dependent photocurrent from other types of spin-split states ........................................ 59
3.6 Summary and future work ........................................ 59

Chapter 4
Spin-dependent photocurrent in topological insulator- magnetic insulator heterostructures 61
4.1 Introduction ........................................ 61
4.1.1 Spin Seebeck effect ........................................ 62
4.1.2 Photo-spin-voltaic effect ........................................ 63
4.1.3 Dirac cone shift in the momentum space ........................................ 65
4.2 Photocurrent measurements in TI-YIG heterostructures ........................................ 66
4.2.1 Field dependent photocurrent ........................................ 66
4.2.2 Longitudinal magneto-optical Kerr effect of YIG ........................................ 68
4.2.3 The influence of the Bi$_2$Se$_3$ seed layer ........................................ 69
4.3 The variation of the field dependent photocurrent with the top gate ........................................ 70
4.4 Unusual features in the hysteresis of the field dependent photocurrent ........................................ 73
4.4.1 Temperature dependence of the photocurrent ........................................ 73
4.4.2 Polarization dependence of the photocurrent ........................................ 73
4.4.3 Chemical potential dependence of the photocurrent under s-polarized light ........................................ 75
4.5 Wavelength dependence of the field dependent photocurrent ........................................ 76
4.6 Underlying mechanism of the field dependent photocurrent ........................................ 77
4.6.1 Discussion of the experimental results ........................................ 77
4.6.2 Longitudinal spin Seebeck effect ........................................ 79
4.6.3 The Dirac cone shift with the in-plane field ........................................ 80
4.6.4 Photo-spin-voltaic effect ........................................ 81
4.6.5 Anomalous Hall effect ........................................ 82
4.7 Summary and future work ........................................ 84

Appendix
Theoretical analysis and numerical calculation of photocurrent 86
1 Theoretical analysis of photocurrent ........................................ 86
1.1 Equation of photocurrent ........................................ 86
1.2 Model Hamiltonian for Bi-chalcogenides ........................................ 88
2 Derivation of optical transition matrix and photocurrent for Bi-chalcogenides ........................................ 94
2.1 $P^+_d$ bulk states ........................................ 95
List of Figures

1.1 Topology in math. The orange and the bowl belong to one topology with genus = 0 while the doughnut and the mug belong to another topology with genus = 1. ................................. 2

1.2 The comparison between the ordinary insulator and the integer quantum Hall state. (a) depicts an insulating state (b) a gapped band structure for the ordinary insulator (c) an object with genus 0 (d) depicts a quantum Hall state (e) Landau levels for quantum Hall state, which can be viewed as a band structure (f) an object with genus 1. Figure reproduced from ref [1]. ............... 3

1.3 The edge states of the quantum Hall insulator (a) The skipping cyclotron orbits at the interface of a normal insulator and a quantum Hall state (b) The electronic structure of a semi-infinite strip from the Haldane model. The single edge state connects the conduction and valence bands. Figure reproduced from ref [1]. .... 4

1.4 The edge states of the quantum spin Hall insulator (a) The up spins and down spins propagate in the opposite direction at the interface of an ordinary insulator and a quantum spin Hall insulator (b) The electronic structure of the two edge states. Figure reproduced from ref [1]. ................................. 5

1.5 Theoretical prediction of the quantum spin Hall insulator. (a) Band structures of HgTe and CdTe. (b) For CdTe/HgTe/CdTe quantum wells, the electron, hole bands are inverted (E1 < H1) for d > 6.3nm; the bands are aligned in the normal order (E1 > H1) for d < 6.3nm. Figure reproduced from ref [2]. ................................. 6
1.6 Experimental realization of the quantum spin Hall insulator. Four probe longitudinal resistance of various HgTe/CdTe quantum wells as a function of the gate voltage with B = 0 T and T= 30 mK. For a normal quantum well I (d= 5.5 nm), the resistance is super high, while for an a quantum well with inverted bands IV (d = 7.3 nm), the resistance reaches a plateau. Figure reproduced from ref [3].

1.7 1D edge state of the QSH insulator translated into 2D surface states of 3D TI. (a) The 1D edge states of the QSH insulator along with the energy dispersion in the momentum space. (b) The 2D surface states of the 3D TI along with the Dirac-cone like dispersion in the momentum space. Figure reproduced from ref [4].

1.8 Crystal structure of Bi$_2$Se$_3$ and the orbital bands from the atomic limit to the crystal (a) The layered crystal structure of Bi$_2$Se$_3$ (b) The p orbital bands of Bi$_2$Se$_3$ under the effect of the chemical bonding (I), crystal-field splitting (II) and spin-orbit coupling (III). Figure reproduced from ref [5].

1.9 Energy and momentum dependence of the local density of states for Bi$_2$Se$_3$ family LDOS around the $\Gamma$ point for (a) Sb$_2$Se$_3$, (b) Sb$_2$Te$_3$, (c) Bi$_2$Se$_3$, (d) Bi$_2$Te$_3$. Figure reproduced from ref [5].

1.10 ARPES measurements of surface electronic band dispersion of Bi$_2$Se$_3$ Electronic band dispersion measured near the $\Gamma$ point along the $\Gamma - M$ (a) and $\Gamma - K$ (b) in the momentum space. Figure reproduced from ref [6].

1.11 Magnetic topological insulators and quantum anomalous Hall effect (a) The gap opening of the Dirac surface states by magnetic impurities (b) Quantized Hall conductance ($e^2/h$) is measured in magnetically doped TI with zero magnetic field at 30 mK. Figure reproduced from ref [7].

1.12 Illustration of the spin Hall effect and Inverse spin Hall effect (a) Illustration of the spin Hall effect. The electrons feel an effective spin-orbit field and get deflected to the transverse direction depending on the spin direction. Opposite spins are deflected to opposite directions. (b) Illustration of the inverse spin Hall effect. The inverse spin Hall effect is a reversed process of spin Hall effect. A spin current generates a transverse charge current. Figure reproduced from ref [8].
1.13 **Spin transfer torque generated by a topological insulator** (a) Schematic of the Bi$_2$Se$_3$ - Permalloy heterostructure and the exerted SOT by passing a current in Bi$_2$Se$_3$ (b) Spin torque ferromagnetic resonance (ST-FMR) measurement in the Bi$_2$Se$_3$ - Py heterostructure. Figure reproduced from ref [9].

1.14 **Spin pumping at the interface of TI-MI** (a) Spin pumping by ferromagnetic resonance driven by microwaves. The spin current is converted into a charge current by the inverse spin Hall effect. (b) Spin pumping by the thermal gradient across the interface. Figure reproduced from ref [10].

1.15 **Polarization dependent photocurrent in Bi$_2$Se$_3** (a) Schematic of the photocurrent generation in Bi$_2$Se$_3$ thin films with circularly polarized light (b) The photocurrent variation with the polarization of light. Figure reproduced from ref [11].

2.1 **Schematic of a typical molecular beam epitaxy system.** Figure from Wikipedia.

2.2 **Illustration of the photo-lithography process.** Figure reproduced from the module of Rice University course CHEM-496.

2.3 **Illustration of the atomic layer deposition.** One cycle of the atomic layer deposition consists of pulsing and purging of one precursor and pulsing, purging of the other precursor (reactant). The number of cycles determines the thickness of the deposited thin films.

2.4 **Illustration of the sputtering.** (a) Photograph of the Kurt Lesker CMS-18 sputtering system in the Materials Research Institute cleanroom. (b) Illustration of the sputtering process.

2.5 **Transmission of the gate material.** Transmission in the wavelength range of 450 nm - 1000 nm.

2.6 **Illustration of the top gate device and band bending induced by the gate.** (a) Schematic of a typical top gate device constructed on top of the topological insulator. (b) Band bending created by a positive gate voltage, the holes are depleted at the surface.

2.7 **Illustration of the optical gating and the chemical potential tuning with light exposure.** The resistance of TI thin films grown on STO can be adjusted by illumination of UV and red light. The UV light raises up the chemical potential of the TI while the red light tunes the chemical potential down. Figure reproduced from ref [12].

xi
2.8 **Comparison between the optical gating and the electrostatic gating.** Each figure contains the variation of the longitudinal resistance and the hall resistance. Figure reproduced from ref [12].

2.9 **Set-up of the photocurrent measurement.** The set-up illustration has included the major components of the photocurrent measurement set-up. Some optical components are skipped here.

2.10 **Three different geometries of MOKE.** (a) Polar MOKE (b) Longitudinal MOKE (c) Transverse MOKE

2.11 **Schematic of the longitudinal MOKE**

3.1 **Experimental set-up of the photocurrent measurement.** Schematic of the excitation and measurement of photocurrent with obliquely incident excitation in the $x-z$ plane. A quarter wave-plate is used to tune the polarization of light and the photocurrent is measured along the $y$-axis.

3.2 **Room temperature polarization dependent photocurrent**
(a) Room temperature photocurrent along the $y$-axis in device A. At $\varphi = 45^\circ$, the laser is left circularly polarized and the photocurrent is negative. At $\varphi = 135^\circ$, the laser is right circularly polarized and the photocurrent is positive. The solid line is a fit to Eq. 3.1. (b) The coefficients $C$, $L_1$, $L_2$, $D$ as extracted from the fit in (a). The amplitude $C$ of the HDPC dominates the polarization dependent photocurrent.

3.3 **Incidence angle dependence of helicity dependent photocurrent**
Photocurrent measured at different incidence angles $\theta$. (a) The normalized amplitude $C_{\text{norm}}$ of the HDPC plotted as a function of $\sin(\theta)$ shows a linear dependence. (b) The normalized amplitude $C_{\text{norm}}$ of the HDPC plotted as a function of $\sin(2\theta)$ shows a poor linear dependence.

3.4 **The directionality of the helicity dependent photocurrent**
(a) The polarization dependent photocurrent in device B. Red and blue scatters denote the photocurrent along each conduction channel and are both fitted to Eq. 3.1 of the main text, denoted by the solid lines. (b) We extracted $C$, $L_1$ and $L_2$ from the Eq. 3.1 along x axis (blue) and y axis (red).
3.5 **Azimuthal angle dependence of the helicity dependent photocurrent** (a) The schematic of the device C, which consists of four conduction channels along different crystal directions. They are noted by the relative angle of the channel direction. The photocurrent along each channel is measured after reorienting the channel along y axis. (b) The polarization dependent photocurrent along each channel. They are fitted to Eq. 3.1 and the extracted HDPC varies less than 10%. 45

3.6 **Four probe resistance at low temperatures** (a) Temperature dependence of four probe longitudinal resistance; $R_{xx}$ shows an insulating behavior. (b) Longitudinal resistance ($R_{xx}$) and the slope of Hall resistance with respect to out of plane magnetic field ($R_{xy}/B$) versus the top gate voltage. The carrier type changes from n to p type at a voltage near 0V. 46

3.7 **Helicity dependent photocurrent in the top gated (Bi$_{1-x}$Sb$_x$)$_2$Te$_3** (a) Picture of the top gate device under the microscope, different parts are labeled. (b) The polarization-dependent photocurrent at different $V_{GT}$ is measured at 15 K in device D. The photocurrents are offset for a better display. We fit the polarization dependent photocurrent at each $V_{GT}$ to Eq. 3.1, denoted by the solid line. (c) Four probe measurement of the longitudinal resistance $R_{xx}$ as a function of the gate voltage, denoted by the red curve. The absolute value $|C|$ of the amplitude of the HDPC is denoted by the blue curve. 47

3.8 **Helicity dependent photocurrent in various Sb doped (Bi$_{1-x}$Sb$_x$)$_2$Te$_3** thin films. From the device D to F, we dope less Sb into Bi$_2$Te$_3$. (a) The gate voltage dependence of the longitudinal resistance $R_{xx}$. The magnitude of $R_{xx}$ in device F (blue curve), taken by a two probe measurement, is much larger than $R_{xx}$ in devices D and E, taken by four probe measurements. Thus, we plot the $R_{xx}$ of device F under a different scale on the right axis of the figure. The different peak positions of $R_{xx}$ in devices D, E and F correspond to the Dirac points of D, E and F, respectively. (b) The gate voltage dependence of the absolute value of the HDPC amplitude– $|C|$. 48
3.9 Photocurrent excited by photons of different wavelength, ranging from 704 nm (1.76eV) to 1000 nm (1.24eV). (a) The polarization-dependent photocurrent at each wavelength, with solid lines showing fits to Eq. 3.1. The curves are vertically offset for clarity. (b) The gate voltage dependence of the HDPC at five different photon energies ranging from 1.24 eV to 1.76 eV. At 1.24 eV, the HDPC is positive and reaches a peak at the voltage corresponding to the Dirac point in the $R_{xx}$ measurement. When we increase the photon energy, the HDPC starts to become negative and finally becomes a valley at 1.76 eV. The valley bottom is also around the Dirac point.

3.10 Photocurrent induced by the bottom surface illumination (a) The polarization dependent photocurrent induced by the illumination on the bottom surface, as compared to the top surface illumination induced photocurrent. The solid curves denoted the fittings to Eq. 3.1. (b) Gate voltage dependent HDPC for both top and bottom illuminations. The HDPC from the bottom surface was not as tunable as the top surface because of the partially screened gating effect at the bottom surface.

3.11 First principles calculation of the bulk band structure of (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$. The irreducible representation to which each bulk band belongs is marked on top of the band. The blue shaded area identifies the energy range which is $\pm 1 - \pm 2$ eV away from the surface Dirac cone, relevant for optical transitions at the photon energy we use.

3.12 Schematic of preferred optical transitions and polar graphs of asymmetric matrix elements of transitions (a) Schematic picture of optical transitions from the bulk valence band to the Dirac surface states. The asymmetric matrix elements for the transitions are plotted in the polar graph of momentum angle ($\theta_k$) for upper and lower Dirac cones (UDC and LDC), where the sign is denoted by the color (red denotes positive and blue denotes negative). The preferred optical transitions are denoted by the red coloring on the Dirac cone. (b) Schematic picture of optical transitions from the Dirac surface states to the conduction band. The asymmetric matrix element is opposite compared to (a).
3.13 **Numerical calculation of the photocurrent.** Calculated photocurrents based on the slab model as a function of the chemical potential. $E_F = 0$ eV denotes the chemical potential located at the Dirac point. The photocurrent contributions from the excited carriers in the surface states (green curve), the bulk bands (blue curve) and the total photocurrent (red curve) are displayed separately.

3.14 **Schematic picture to explain the peak of HDPC at the Dirac point.** (a), (b) and (c) denote the chemical potential below, near and above the Dirac point, respectively. The red dotted arrows denote the preferred transitions from the surface states to conduction bands ($s \rightarrow c$) while the blue dotted arrows denote the preferred transitions from the valence bands to surface states ($v \rightarrow s$). The two transitions happen simultaneously and rely on the position of the chemical potential. (a) The chemical potential is below the Dirac point. The excited carriers are denoted by filled circles (electrons) and empty circles (holes). In the valence band, the excited holes are separated into two parts, one denoted by small circles and the other denoted by large circles. As shown in the sub-diagram, the small circles are distributed evenly around the $\Gamma$ point, leading to zero total generated photocurrent. Only the large circles contribute to the net photocurrent. The net photocurrent induced by the bulk carriers is along the negative $y$ direction and denoted by the arrows pointing to the left. The length of the arrows denotes the magnitude of the photocurrent. (b) The chemical potential crosses the Dirac point. The length of the arrows reach a maximum indicating the largest photocurrent. (c) The chemical potential is above the Dirac point. The excited carriers in the conduction band are separated into two parts and the small circles do not contribute a net photocurrent. Therefore, the length of the arrows denoting the net photocurrent decreases.

3.15 **Numerical calculation of photocurrent using different relaxation times for surface and bulk bands** (a) Photocurrent for the case with $\tau_s = 0.5\tau_v$. $\tau_s$, $\tau_c$ and $\tau_v$ denote the relaxation time of the surface states, conduction band and valence band respectively. (b) Photocurrent for the case with $\tau_s = \tau_v$. (c) Photocurrent for the case with $\tau_s = \tau_v$.

4.1 **Schematic illustrations of the spin Seebeck effect** (a) Longitudinal spin Seebeck effect (b) Transverse spin Seebeck effect. Figure reproduced from ref [13].
4.2 Schematic illustrations of the photo-spin-voltaic effect (a) Schematic of the spin injection induced by light illumination (b) Detailed spin injection process due to the electron and hole diffusion imbalance. Figure reproduced from ref [14]. .................................................. 65

4.3 Schematics of the Dirac cone shift by the in-plane magnetization (a) The surface states dispersion without the Zeeman field. (b) The surface states dispersion with the Zeeman field induced by the in-plane magnetization. Figure reproduced from ref [15]. .... 66

4.4 Schematic of the optical transition between the shifted Dirac cone and the bulk conduction band. The excited electrons in the bulk band are not symmetric around Γ point, thus inducing a net momentum. ................................................................. 67

4.5 Field dependent photocurrent in the TI-YIG heterostructure. (a) Schematic of the photocurrent measurement with an in-plane magnetic field in the TI-YIG heterostructure. (b) Photocurrent in device A at room temperature (293 K) and 25 K as a dependence of the in-plane magnetic field. ................................. 68

4.6 Longitudinal MOKE of the YIG layer in device A (a) The longitudinal Kerr rotation of the YIG thin film at room temperature (293 K). (b) The longitudinal Kerr rotation of the YIG thin film at 25 K. ................................................................. 69

4.7 Field dependent photocurrent in device B without the Bi$_2$Se$_3$ seed layer. (a) Photocurrent in device B at room temperature (293 K) as a dependence of the in-plane magnetic field. (b) Field dependent photocurrent at 25 K. .................................................................................. 70

4.8 Field dependent photocurrent varies with the top gate. (a) The Hall resistance (red curve) and the extracted 2D carrier concentration ($n_{2D}$) as a function of the top gate voltage. (b) Field dependent photocurrents at 25 K at variable gate voltages ranging from 10 V to -8 V. (c) The saturated photocurrent at a large positive field (blue) and the slope of the linear dependence of photocurrent at large fields (red) as a function of the gate voltage. .......... 71

4.9 Field dependent photocurrent in device B with variable gate voltages. (a) The longitudinal resistance ($R_{xx}$) as a function of the top gate voltage. (b) Field dependent photocurrents at 25 K under variable gate voltages ranging from 10 V to -12 V. (c) The saturated photocurrent at a large positive field (blue) and the slope of the linear dependence of photocurrent at large fields (red) as a function of the gate voltage. ........................................ 72
4.10 **The variation of the field dependent photocurrent with temperature.** The photocurrent with p-polarized light at various temperatures. The unusual features of the hysteresis disappeared at 130K. .................................................. 74

4.11 **Field dependent photocurrents at different polarizations.** (25K) The photocurrents induced by p-polarized, circularly polarized and s-polarized light. The top right panel shows the Kerr rotation of YIG on the same piece of sample. ...................... 75

4.12 **Field dependent photocurrent under different polarizations at 130K.** The photocurrents induced by p-polarized and s-polarized light at 130K. .......................................................... 75

4.13 **Gate voltage dependence of the photocurrent under s-polarized light.** The field dependent photocurrent induced by s-polarized light varies with the gate voltage. The direction of the hysteretic change reverses direction as that of the p-polarized light induced photocurrent. .................................................. 76

4.14 **The gate voltage dependence of the saturated photocurrent under different wavelengths.** The saturated photocurrent under 480 nm, 580 nm, 700 nm and 950 nm light illumination as a function of the gate voltage. .................................................. 78

4.15 **The LSSE study in TI-YIG heterostructures from ref [16].** (a) Temperature dependence of longitudinal resistance $R_{xx}$ for $(\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3$ -YIG heterostructures with $x$ ranging from 0 to 1. (b) The LSSE signal in $(\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3$ -YIG heterostructures (with different Sb ratios) as a function of the in-plane field. The direction of the hysteresis did not change with the chemical potential tuning. ...... 80

4.16 **Schematic of optical excitations in topological insulators under different wavelengths.** The excitation under 480nm light are denoted by the blue arrow while the excitation under 950nm light is denoted by the red arrow. .................................................. 83

4.17 **Demonstration of sensing the magnetization by the photocurrent measurement.** When pulsing the magnetic field, the magnetization of YIG is oriented. Correspondingly, an non-zero photocurrent is observed. The direction of the photocurrent depends on the direction of the magnetic field. ........................................... 85
List of Tables

4.1 Consistency of the experimental results with different mechanisms . 84
List of Symbols

\( \mathcal{H} \) Hamiltonian
\( R \) Resistance
\( R_{xx} \) Longitudinal resistance
\( R_{xy} \) Hall resistance
\( T \) Temperature
\( V_{GT} \) Top gate voltage
\( g \) genus
\( \varphi \) Angle between the fast axis of quarter-wave plate and the polarization of light
\( \theta \) Incidence angle of light
\( \theta_{ST} \) Spin Hall angle
\( C \) Circular photo-galvanic effect coefficient
\( L_1, L_2 \) Linear photo-galvanic effect coefficient
\( D \) Offset photocurrent
\( \tau_{ps} \) Relaxation time
\( B_{in} \) In-plane magnetic field
\( n_{2D} \) 2D carrier concentration
List of Acronyms

1D, 2D, 3D  One-Dimensional, Two-Dimensional, Three-Dimensional
TI    Topological Insulator
TSS   Topological Surface State
TRS   Time reversal Symmetry
QSH   Quantum Spin Hall
SOC   Spin-Orbit Coupling
QHE   Quantum Hall effect
QSHE  Quantum spin Hall effect
QAHE  Quantum Anomalous Hall effect
HDPC  Helicity dependent photocurrent
CPGE  Circular Photo-galvanic effect
LPGE  Linear Photo-galvanic effect
PDE   Photon drag effect
TKNN  Thouless-Kohmoto-Nightingale-den Nijs
QW    Quantum Well
MI    Magnetic insulator
STT   Spin-transfer torque
HM    Heavy metal
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTJ</td>
<td>Magnetic tunnel junctions</td>
</tr>
<tr>
<td>MRAM</td>
<td>Magnetic random-access memory</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local density of states</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-Resolved PhotoEmission Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>MOKE</td>
<td>Magneto-optical Kerr effect</td>
</tr>
<tr>
<td>RKKY</td>
<td>Ruderman-Kittel-Kasuya-Yosida</td>
</tr>
<tr>
<td>(L)SSE</td>
<td>(Longitudinal) Spin-Seebeck effect</td>
</tr>
<tr>
<td>PVE</td>
<td>Photo-voltaic effect</td>
</tr>
<tr>
<td>QL</td>
<td>Quintuple layer</td>
</tr>
<tr>
<td>QWP</td>
<td>Quarter wave-plate</td>
</tr>
</tbody>
</table>
First and foremost, I would like to express my sincere gratitude to my advisor, Prof. Nitin Samarth. Everything that is valuable in this dissertation must be attributed to him. I have had such an amazing journey working under his advise. His knowledge and enthusiasm in physics, encouragement for new ideas, tolerance and patience for failures have guided me through the good and bad times of my Ph. D. I am so grateful for the freedom he granted during my research. He taught me the most important thing: working independently and shouldeering the responsibility of your research. His positive outlook on viewing failures and excitement for new physics have deeply inspired me, and will keep influencing me in the future.

I would like to thank Professor Chao-xing Liu for giving theoretical support for my experiment and all the inspiring discussions in his office. I am also grateful to Professor Jun Zhu, Chao-xing Liu and Venkatraman Gopalan for serving as my dissertation and comprehensive exam committees.

I would also like to thank my group members and colleagues. Many thanks to Dr. Anthony Richardella for such a long time of collaboration. He is always generous in offering help and ideas. I am so grateful for the guide from Dr. Kriti Kohli during my first two years of Ph. D. I learned everything needed for becoming an experimentalist from her. I would like to thank Dr. Duming Zhang, Dr. Abhinav Kandala, Dr. Joon Sue Lee and Dr. Andrew Balk for instructing and teaching me new things in the lab and giving me suggestions on experiments. Many thanks to Timothy Pillsbury and a previous group member, Bing Yao for working with me in the lab from day to night. The ideas we exchanged, the experiments we conducted together made me where I am. I would also like to thank James Kally and Dr. Hailong Wang for the MBE growth; Di Xiao for helping me with Heliox and supporting me as a friend; and the rest of my labmates, Susan Kempinger, Dr. Robert Fraleigh, Eric Kamp, Thomas Flanagan for both professional and personal helps. I had a wonderful time working with you all.

I would like to express my gratitude to collaborators outside of Penn State. Many thanks to Dr. Andrew Yeats for running the spatial resolved photocurrent measurement, the optical gating, spatial resolved MOKE for and with me. I really
treasured the experience working in your lab. I would also like to thank Yunqiu (Kelly) Luo for running the wavelength tunable photocurrent measurement for me day and night. I would like to thank Prof. Roland Kawakami and Prof. David Awschalom for the collaboration with me.

Last but not least, I want to give thanks to all my friends at Penn State - Xiaomei Zhang, Chao Tian, Xiaoyan Zhang, Sumithra Surendralal, Aruna Kesavan, Hsiu-Chuan Hsu, Jing Li, Junjie Wang, etc - who accompany me and give me support during these years. I would like to thank my parents for their love and endless support in my pursuits. I would give my special thanks to my dear husband, Qingze Wang for loving, supporting and encouraging me. His love refreshes me every day and makes me keep fighting and smiling. Life is wonderful because all of you.
Dedication

To my parents and Qingze
Chapter 1
Introduction

1.1 Topology in condensed matter

In the history of condensed matter physics, one of the major topics is to discover and classify distinctive phases of matter. Until the early 1980’s, it was believed that phases can be characterized in terms of underlying symmetries that are spontaneously broken. Explicitly, the loss of one symmetry results in one kind of ordering phases. The phase transition between the liquid and crystalline solid is one simple example. This transition is marked by the breaking of the continuous translational symmetry. Other phases, like ferromagnets and superconductors, are characterized by broken time reversal and gauge symmetries. However, the observation of the quantum Hall state in 1980 [17] was the first example that has no corresponding symmetry breaking. This discovery has led to a different classification paradigm, which is not based on the symmetry, but the notion of topological order. By a topological classification, an integer property can be assigned to the quantum mechanical system that is insensitive to smooth changes in system parameters, unless a quantum phase transition happens. In other words, the integer property is topologically protected.

1.1.1 What is topology?

Before delving into the topological phases in condensed matter, let’s take a quick review of the idea of topology in mathematics. Topology refers to a branch of mathematics that deals with the geometric properties of shapes. If under a smooth deformation, one shape can be transformed to another, these two shapes have the same topology. A smooth deformation refers to a continuous change of the shape
without the creation or annihilation of holes. Fig. 1.1 shows a simple example of two categories of objects. The orange and the bowl belong to one topology while the doughnut and the mug belong to another topology. An integer property can be assigned to each topology, which does not change during a smooth deformation. This integer is called genus, which is a topological invariant. The Gauss-Bonnet theorem relates the surface integral of the Gaussian curvature to the genus by:

\[ \int_{\mathcal{S}} \kappa dA = 4\pi (1 - g), \]

where \( \kappa \) is the Gaussian curvature, \( g \) is the genus. Thus, for the orange or bowl, the genus is zero, while for the doughnut or the mug, the genus is 1. For topology in condensed matter, the major task is to find the analogues to the Gaussian curvature and the genus (topological invariant).

1.1.2 Topological invariant for gapped band structures

As mentioned above, the first example of a phase that can not be classified by the symmetry breaking is the integer quantum Hall state. Thouless, Kohmoto, Nightingale and den Nijs (TKNN) [18] found that topology was the key to distinguish the quantum Hall state from the ordinary insulator. For a crystalline solid, the
band theory exploits the translational symmetry to classify electronic states in terms of the crystal momentum \( \mathbf{k} \). The Bloch states \( |u_m(k)\rangle \) are eigenstates of the Bloch Hamiltonian \( \mathcal{H}(k) \). For the ordinary insulating state and the integer quantum Hall state, the band structures are gapped, as shown in Fig. 1.2. The topological classification for the gapped band structures is based on the equivalence classes of \( \mathcal{H}(k) \) under the continuous deformation without closing the band gap. The analogues to the Gaussian curvature and the genus are the Berry curvature and the Chern number. The Berry curvature is defined as \( \nabla \times (i \langle u_m | \nabla_k | u_m \rangle) \) and the Chern number is the integral of the Berry curvature in the Brillouin zone divided by \( 2\pi \). The Chern number, which is an integer, is the topological invariant that can classify the topological phases for gapped band structures. For the ordinary insulator, the Chern number is zero while for the integer quantum Hall state, the Chern number is \( n \). (\( n \) equals to how many landau levels are occupied.)

Figure 1.2. The comparison between the ordinary insulator and the integer quantum Hall state. (a) depicts an insulating state (b) a gapped band structure for the ordinary insulator (c) an object with genus 0 (d) depicts a quantum Hall state (e) Landau levels for quantum Hall state, which can be viewed as a band structure (f) an object with genus 1. Figure reproduced from ref [1].

### 1.1.3 Bulk-boundary correspondence and the edge states

At the interfaces of two gapped states where the topological invariant changes, gapless conducting edge states would appear. This is called the bulk-boundary
correspondence. This is easy to understand in terms of the gap closing. Imagine an interface between a trivial insulator and a quantum Hall state, when the crystal slowly interpolates as a function of distance $z$ ($z$ is along the perpendicular direction of the interface), somewhere along the way the gap has to close since the topological invariant changes. Therefore, there will be electronic states bound to the interface where the gap passes through zero. The edge states in the quantum Hall insulator is an example. Though the edge states can be described by the skipping motion of electrons’ cyclotron orbits bouncing off the edge, the change of the topological invariant from zero to $n$ is the deeper reason why the edge states have to appear. A schematic of the edge state in the quantum Hall insulator is shown in Fig. 1.3 along with the energy dispersion of the edge state in the momentum space.

Figure 1.3. The edge states of the quantum Hall insulator (a) The skipping cyclotron orbits at the interface of a normal insulator and a quantum Hall state (b) The electronic structure of a semi-infinite strip from the Haldane model. The single edge state connects the conduction and valence bands. Figure reproduced from ref [1].

1.2 Topological insulators

The quantum Hall state is only accessible with a large magnetic field that breaks the time reversal symmetry. In the past ten years, new topological phases have emerged in condensed matter physics, called topological insulators. [3,5,6,19–21] Unlike the quantum Hall state, the topological insulator (TI) does not need a magnetic field. Instead, a strong spin-orbit coupling (SOC) leads to the topologically distinct state. A TI has a gapped band structure similar to the ordinary insulator, however, a $\mathbb{Z}_2$ topological invariant [22] (0 or 1) can be used to distinguish the two states.
1.2.1 2D topological insulator

2D TIs are also known as quantum spin Hall (QSH) insulators. The edge states of the QSH insulator are different from that of the quantum Hall insulator. As shown in Fig. 1.4, the edge states have unique "spin-filtered" property. Carriers with up spins propagate in one direction, while the down spins propagate in the opposite direction. These edge states are protected by the time reversal symmetry (TRS), where the back-scattering is prohibited. The search for the QSH insulator was initiated in graphene [23], but the weak spin-orbit coupling in graphene was an obstacle. A better place to look for the QSH insulator would be in materials made from heavy elements with strong spin-orbit interactions.

Figure 1.4. The edge states of the quantum spin Hall insulator (a) The up spins and down spins propagate in the opposite direction at the interface of an ordinary insulator and a quantum spin Hall insulator (b) The electronic structure of the two edge states. Figure reproduced from ref [1].

1.2.1.1 HgTe/CdTe quantum well

In 2006, Bernevig, Hughes and Zhang predicted the existence of the QSH insulator in HgTe/CdTe quantum wells. [2] One year after the prediction, an experimental observation of the 2D TI was reported in the HgTe/CdTe quantum well. [3]

The band inversion is a prerequisite for the topologically nontrivial phase. For the CdTe/HgTe/CdTe quantum well, the barrier material CdTe has a normal band structure of s-type $\Gamma_6$ band lying above the p-type $\Gamma_8$ band, as shown in Fig. 1.5(a). The two bands, separated by a large energy gap, are the conduction band and valence band receptively. For the well material HgTe, due to the strong
spin-orbit coupling, the p-type $\Gamma_8$ band (the hole band) is raised above the s-type $\Gamma_6$ band (the electron band). The normal bands are inverted. However, the band structure of HgTe can be tuned by the width of the quantum well. For a narrow quantum well (thickness of HgTe ($d < 6.3\, \text{nm}$)), the quantum confinement is strong enough to shift the energy bands. The hole band and the electron band of HgTe would be aligned to the normal ordering, the electron band lying above the hole band. Whereas, for a wide quantum well ($d > 6.3\, \text{nm}$), the energy bands of HgTe would keep inverted, as shown in Fig. 1.5. Therefore, the 2D TI only exists in CdTe/HgTe/CdTe quantum well when the thickness of HgTe is less than 6.3 nm.

![Figure 1.5. Theoretical prediction of the quantum spin Hall insulator. (a) Band structures of HgTe and CdTe. (b) For CdTe/HgTe/CdTe quantum wells, the electron, hole bands are inverted ($E_1 < H_1$) for $d > 6.3\, \text{nm}$; the bands are aligned in the normal order ($E_1 > H_1$) for $d < 6.3\, \text{nm}$. Figure reproduced from ref [2].](image)

Within a year of the theoretical prediction, the group led by Laurens Molenkamp reported the first experimental realization of the 2D quantum spin Hall insulator in HgTe/CdTe quantum wells grown by molecular beam epitaxy. The width of the quantum wells ranged from 5.5 nm to 12 nm. A gate was used in each device to tune the Fermi level through the gap. As shown in Fig. 1.6, the conductance of the quantum well varied with the thickness of HgTe (I-IV). For quantum wells
II, III and IV, the bands were inverted, leading to a quantized conductance $2e^2/h$ associated with the two edge states. However, for quantum well I, the bands had a normal ordering, thus the conductance was very low. The experimental observation of the 2D QSH insulator marked the birth of the 2D TI.

**Figure 1.6. Experimental realization of the quantum spin Hall insulator.** Four probe longitudinal resistance of various HgTe/CdTe quantum wells as a function of the gate voltage with $B = 0$ T and $T= 30$ mK. For a normal quantum well I (d = 5.5 nm), the resistance is super high, while for an a quantum well with inverted bands IV (d = 7.3 nm), the resistance reaches a plateau. Figure reproduced from ref [3].

### 1.2.2 3D topological insulator

Soon after the discovery of the 2D TI, three theoretical groups independently reported the generalization of the quantum spin Hall insulator to three dimensions. [24–26] The term "topological insulator" was first put up by Moore and Balents [25] to describe the 3D TRS protected topologically nontrivial state. Various predictions of 3D TIs were made in materials like the semiconductor alloy Bi$_{1-x}$Sb$_x$, α-Sn and HgTe under uniaxial strain. Soon after, the first 3D TI was experimentally observed in Bi$_{1-x}$Sb$_x$ by Hsieh’s group. [21] The surface structure of Bi$_{1-x}$Sb$_x$ was quite complicated and the band gap was very small. A search for candidates of 3D TIs with a larger band gap and simpler surface structure was initiated, which led
to the second generation of 3D TIs. Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ were identified as 3D TIs both theoretically [5, 6] and experimentally. [6, 27–29]

![Figure 1.7](image)

**Figure 1.7. 1D edge state of the QSH insulator translated into 2D surface states of 3D TI.** (a) The 1D edge states of the QSH insulator along with the energy dispersion in the momentum space. (b) The 2D surface states of the 3D TI along with the Dirac-cone like dispersion in the momentum space. Figure reproduced from ref [4].

A naive interpretation of the 3D TI is to think of a stack of non-interacting 2D QSH insulators. The 1D edge state can be extended to 2D surface states. Due to the discontinuity of the $Z_2$ invariant at the surface, the surface states are gapless states as well. Like the QSH insulator, the surface states of the 3D TI have the unique spin-momentum locked property. As shown in Fig. 1.7, the linearly dispersed edge state of the QSH insulator which connects the conduction and valence band(a) would translate into a 2D, graphene-like "Dirac cone" (b). The surface states can be described by the following Hamiltonian:

$$H = A(\sigma_x k_y - \sigma_y k_x).$$  \hspace{1cm} (1.2)
1.2.2.1 Bi$_2$Se$_3$ family

Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$ are the most well known 3D topological insulators. They all have the rhombohedral crystal structures with space group $D_{3d}^{5}$. Taking Bi$_2$Se$_3$ as an example, the layered structure consists of alternating bismuth and selenium atomic layers as shown in Fig. 1.8(a). Within the box marked in the figure, five atomic layers construct a quintuple layer. Within one quintuple layer, the coupling between two atomic layers is strong, while the coupling between two quintuple layers, dominated by the van der Waals force, is much weaker. Therefore, synthesis of these materials by molecular beam epitaxy are rather easy despite of lattice mismatch with the substrate.

![Crystal Structure of Bi$_2$Se$_3$ and the Orbital Bands from the Atomic Limit to the Crystal](image)

**Figure 1.8.** Crystal structure of Bi$_2$Se$_3$ and the orbital bands from the atomic limit to the crystal (a) The layered crystal structure of Bi$_2$Se$_3$ (b) The p orbital bands of Bi$_2$Se$_3$ under the effect of the chemical bonding (I), crystal-field splitting (II) and spin-orbit coupling (III). Figure reproduced from ref [5].

The band inversion, which makes the material topologically nontrivial, is induced by the strong spin-orbit coupling in Bi$_2$Se$_3$, Bi$_2$Te$_3$ or Sb$_2$Te$_3$. Fig. 1.8(b) shows the evolution of the Bi and Se orbital bands with the effect of crystal-field splitting and spin-orbit coupling. In stages (I) and (II), the orbital bands hybridize, shift and split by the chemical bonding and crystal-field splitting. In the last stage (III),
the spin-orbit coupling induces the band inversion of the p orbitals. Zhang, Liu et.al calculated the surface states of the Bi$_2$Se$_3$ family on the basis of an ab initio calculation. As shown in Fig. 1.9, the Dirac-cone like surface states were present in Sb$_2$Te$_3$ (b), Bi$_2$Se$_3$(c) and Bi$_2$Te$_3$ (d) around the $\Gamma$ point, whereas no surface states for Sb$_2$Se$_3$ (a). The unusual surface states were also identified experimentally in Bi$_2$Se$_3$ by angle-resolved photoemission spectroscopy (ARPES) [6], as shown in Fig. 1.10. The inverted bulk band gap was approximately 0.3 eV ($\sim$ 3480 K), making Bi$_2$Se$_3$ a topological insulator even at room temperature. The arrows in the figure point to the charge neutrality point, called Dirac point, which is exposed in the band gap.

Figure 1.9. Energy and momentum dependence of the local density of states for Bi$_2$Se$_3$ family LDOS around the $\Gamma$ point for (a) Sb$_2$Se$_3$, (b) Sb$_2$Te$_3$, (c) Bi$_2$Se$_3$, (d) Bi$_2$Te$_3$. Figure reproduced from ref [5].

1.2.2.2 Exotic physics of the Dirac surface states

The surface states, like the edge states in QSH insulator, are topologically protected from non-magnetic disorders. The two major properties of the surface states are the spin-momentum locking (Fig. 1.7(b)) and the TRS protection from the back scattering. The surface states of 3D TIs are not spin-degenerate, instead, TRS requires that the spin reverses direction when momentum changes from $\mathbf{k}$ to $-\mathbf{k}$. The
Figure 1.10. ARPES measurements of surface electronic band dispersion of Bi$_2$Se$_3$. Electronic band dispersion measured near the $\Gamma$ point along the $\Gamma - M$ (a) and $\Gamma - K$ (b) in the momentum space. Figure reproduced from ref [6].

spin direction and the momentum direction are locked perpendicularly to each other. Thus, the spin polarized surface states may be utilized in spintronics applications. The next section will give an introduction of the topological spintronics.

While the TRS protected surface states are interesting by its own, exotic physics arising from symmetry breaking in 3D TIs have attracted much attention. For instance, interfacing 3D TIs with superconductors breaks the gauge symmetry and sets a platform for the creation of Majorana zero-mode, which opens a new field of realizing fault-tolerant topological quantum computing. [30,31]. Another important direction of the 3D TIs’ research is to break the time reversal symmetry by introducing magnetism into the system. The external magnetism can open a gap for the Dirac surface states at the $\Gamma$ point (Fig. 1.11(a)), leading to many exciting new physics. There are proposals of quantum Hall effect with zero field (quantum anomalous Hall), [32] topological magneto-electric effect, [33] magnetic monopoles [34] and so on. Among these, the quantum anomalous Hall effect (QAHE) has been experimentally realized in various magnetically doped 3D TIs. [7,35,36]

They utilized electrostatic gatings to tune the chemical potential into the gap at the Dirac point induced by the exchange coupling. In the gap, the surface conduction
along with the bulk conduction were frozen at very low temperatures, whereas a dissipationless edge state dominates the conduction. Therefore, a quantized Hall conductance was observed in this region, as shown in Fig. 1.11(b). This edge state is similar to the edge state of the quantum Hall insulator, however, no magnetic field is needed for QAHE.

1.3 Topological insulator- magnetic insulator heterostructures

Heterostructures that combine TIs with magnetic materials have attracted much attention recently. Both the time reversal symmetry and inversion symmetry are broken at the interfaces of TIs and magnetic materials. Interfacing with magnetic materials provides another approach for gap opening in Dirac surface states. The advantages of this method over the magnetic doping include uniform exchange coupling at the surface, preservation of the TI’s crystalline structure, etc. Besides exotic phenomena induced by the magnetic proximity effect, another application of
the heterostructure is in spintronics which utilizes spins for information processing. In this context, using magnetic insulators in the heterostructure is particularly relevant.

### 1.3.1 Topological spintronics

Spintronics is a field of electronics, which utilizes another degree of freedom-electron spin. The control and manipulation of spins could lead to potential applications of using spin to store information. One well-known example is the magnetoresistive random-access memory (MRAM) which uses the magnetic tunnel junctions (MTJs). The goal of spintronics is to achieve non-volatile memory and logic devices with fast speed, high density and low energy consumption. One major challenge of reaching this goal is to incorporate novel materials into the magnetic structures for manipulation and switching of the magnetic moment. A new technique of magnetization switching that attracts much attention is using spin transfer torque (STT). [37] If electrons carry net spins and flow into a magnetic layer that has an non-parallel magnetization, the current will develop a torque exerted on the magnetization. As a consequence, the magnetization is altered and change direction. This kind of switching is called 'spin transfer switching'.

#### 1.3.1.1 Spin-orbit transfer torque

Traditional STT switching is realized in MTJs, a stack of ferromagnetic metal/insulator/ferromagnetic metal. The magnetization of one ferromagnetic metal layer is fixed and serves as a spin filter to generate a spin-polarized current that passes through this layer. The other magnetic metal layer serves as a free layer where the information is stored. The incident spin-polarized current can exert STT on the free layer and changes its magnetization. However, the STT switching needs a large current passing through the MTJ which may break down the barrier layer after frequent uses. To circumvent this problem, spin orbit torques (SOT) generated by materials with strong spin-orbit couplings have become an alternative spin transfer switching. In particular, heavy metals (HMs) have been integrated to realize the SOT switching using the spin Hall effect (SHE). In this case, the spin transfer torque is not generated by passing a current across the MTJ, instead, a lateral current inside the HM is applied. During the past few years, this research field has
earned tremendous success. [38–41]

Let’s take a closer look at the generation of SOT by applying a lateral current inside the HM. For materials with strong spin-orbit couplings, the spin and the orbital momentum are highly correlated. For a charge current through the high SOC material, the electrons will feel an effective spin-orbit field which can deflect the electrons. The direction of the spin-orbit field depends on the electron’s spin direction, thus opposite spins will be deflected to opposite directions inducing a transverse spin current. (Fig. 1.12(a)) This is called spin Hall effect. Therefore, a lateral charge current applied in the HM can generate a transverse spin current. A reversed process could happen as well, in which a spin current induces a transverse charge current, referred as "inverse spin Hall effect". (Fig. 1.12(b))

![Figure 1.12. Illustration of the spin Hall effect and Inverse spin Hall effect](image)

(a) Illustration of the spin Hall effect. The electrons feel an effective spin-orbit field and get deflected to the transverse direction depending on the spin direction. Opposite spins are deflected to opposite directions. (b) Illustration of the inverse spin Hall effect. The inverse spin Hall effect is a reversed process of spin Hall effect. A spin current generates a transverse charge current. Figure reproduced from ref [8].

### 1.3.1.2 The birth of topological spintronics

Heavy metals are not the only materials that can generate effective SOT. 3D TIs are good candidates for SOT based spintronics as well. Besides the large spin-orbit coupling, 3D TIs hold the spin-momentum locked surface states, which make an additional contribution to SOT. In 2014, the research led by Dan Ralph’s group [9] reported that a 3D TI Bi$_2$Se$_3$ could generate SOT to the adjacent magnetic metal (Py) with much better efficiency as compared to heavy metals. An illustration of SOT in the TI-Py heterosture is shown in Fig. 1.13(a). A current induced SOT
was measured by using a spin torque ferromagnetic resonance technique, as shown in Fig. 1.13(b). The spin Hall angle ($\theta_{ST} = \frac{2e}{\hbar} J_s / J_c$) of Bi$_2$Se$_3$ was extracted from this measurement and compared to heavy metals. This experiment and a few more others [42–44] marked the birth of topological spintronics, in which 3D TIs were interfaced with magnetic metals.

Figure 1.13. Spin transfer torque generated by a topological insulator (a) Schematic of the Bi$_2$Se$_3$ - Permalloy heterostructure and the exerted SOT by passing a current in Bi$_2$Se$_3$ (b) Spin torque ferromagnetic resonance (ST-FMR) measurement in the Bi$_2$Se$_3$ - Py heterostructure. Figure reproduced from ref [9].

1.3.2 Interfacing topological insulators with magnetic insulators

Previous studies of topological spintronics have utilized ferromagnetic metals in the heterostructure of TI-magnetic materials. The current induced SOT is impeded by the shunting current in the conducting ferromagnet. To circumvent this problem, magnetic insulators can be incorporated to replace the ferromagnetic metal. Extensive studies have been carried out for topological insulator- magnetic insulator (MI) heterostructures, in which magnetic insulators are EuS [45], yttrium iron garnet (YIG) [10,46], BaM [47], MnSe [48] etc. Most of the experiments or theoretical work focus on the magnetic proximity effect at the interface of the TI and MI. Very few [10] studied the spin transport at the interface of TI-MI. Understanding the magnetic proximity effect is of fundamental importance for exploring interesting physics arising from the TRS breaking. Whereas, a study of the spin transport at the interface is critical for spintronics applications.
1.3.2.1 Magnetic proximity effect at the interface of TI and MI

The magnetic proximity effect arises from exchange coupling induced spin and orbital susceptibility in the non-magnetic layer. Due to the short range nature of the exchange coupling, the first layer of magnetic ions in MI at the interface dominates the exchange coupling. Thus for a ferrimagnetic insulator (such as YIG) or an antiferromagnetic insulator (such as MnSe), it provides the same form of ferromagnetic exchange coupling, just like a ferromagnetic insulator (such as EuS). Theoretical interpretations \[48,49\] of the magnetic proximity effect usually employ the first-principles calculations to study the electronic structures at the interface. The first principles calculations of Bi\(_2\)Se\(_3\) - MnSe heterostructures show that the charge redistribution and the mixing of the TI orbitals and the MI orbitals induce modifications of the electronic structure near the interface. An interfacial ordinary state emerges right at the interface, whereas the topological state is located further from the interface (the second QL). Thus, the exchange coupling between the MI and the TI is mediated by the interfacial state. Moreover, the band bending at the interface could greatly alter the interfacial state. Another theoretical work discovers that the magnetic proximity is very sensitive to the gap between the MI and TI. A few angstroms of gap (like defects at the interface) could cause a significant decay of the exchange coupling. Therefore, the magnetic proximity effect at the interface of TI and MI is easily affected by the interface quality.

Despite of the success of using first principles calculations, a complete determination of interfacial magnetic structures remains challenging. The theory work by Moodera’s group \[50\] at MIT bypassed this problem by studying the interlayer exchange coupling of two MIs separated by a TI thin film. They showed that the electronic states at the TI-MI interface could be identified through the indirect coupling between the two MIs. Distinctive coupling behaviors between the Dirac surface state and the p orbital bands of Bi and Se were discovered. The coupling between the TI surface state and the MI caused the paramagnetic susceptibility while the coupling between the orbital bands from the bulk and the MI induced the diamagnetic susceptibility. Thus, it is suggested that the chemical potential tuning can greatly alter the exchange coupling between the TI and MI.

Most of the previous theoretical approaches studied the MI with an out-plane magnetization. A gap opening at the Dirac point of the surface states were proposed. For the MI with an in-plane magnetization, very limited work \[48\] has
been conducted. It is proposed that the Dirac cone is shifted in the momentum space and no gap opening is present at the Dirac point for the in-plane magnetism. Thus, the MI with an in-plane magnetization is not suitable for the exploration of exotic phenomena like the quantum anomalous Hall. However, the heterostructure of TI-MI based on the MI with an in-plane magnetic anisotropy is still useful for the spintronics applications.

Besides various theoretical approaches, there are many experimental explorations [45,46] of the magnetic proximity effect at the interface of TI and MI. However, traditional techniques for magnetization measurements face challenges. Though APRES is very powerful for measuring spin-resolved surface electronic and magnetic structures, the short escape depth of the photo-electrons make it inapplicable to study the interfacial magnetic properties of the TI-MI heterostructure. Magneto-optical Kerr effect (MOKE) is limited for the interface study as well since it measures the overall magnetization up to tens of nanometers’ thickness. Another powerful technique, polarized neutron reflectometry (PNR), has proven its success in studying the in-plane magnetization with depth profiling. However, it is not suitable for measuring the out-of-plane magnetization. Therefore, exploring new techniques of magnetization measurements for the TI-MI heterostructure is necessary.

1.3.2.2 Spin pumping at the interface of TI-MI

Very limited experimental work of spin pumping has been conducted at the interface of TI-MI. The spin pumping is driven by either the ferromagnetic resonance (FMR) [10] (Fig. 1.14(a)) or the thermal gradient. [16](Fig. 1.14(b)) Directly using an electrostatic voltage to drive a current across the TI-MI interface is not applicable since the MI is insulating. The FMR arises from the precession of the magnetization in an external magnetic field. When the precession frequency matches with the microwave frequency, absorption of the microwave increases sharply, which is called ferromagnetic resonance. For the spin pumping induced by a thermal gradient, there is a name for this effect - spin Seebeck effect (SSE). More background introduction of SEE can be found in Chapter 4. For either kind of spin pumping, the vertical spin current is converted into a charge current by the inverse spin Hall effect in the TI. Thus, the spin pumping can be easily probed by a transverse voltage or current measurement in the TI.
Figure 1.14. Spin pumping at the interface of TI-MI (a) Spin pumping by ferromagnetic resonance driven by microwaves. The spin current is converted into a charge current by the inverse spin Hall effect. (b) Spin pumping by the thermal gradient across the interface. Figure reproduced from ref [10].

1.4 Photo-galvanic effect

The generation and investigation of spin polarization in topological insulators is the main topic of this dissertation. One powerful method is to use polarized light to create excitations. Photo-galvanic effect refers to the photocurrent generation by a polarized light under uniform illumination without external bias. The photo-galvanic effect usually requires a low spatial symmetry of the crystal and was first discovered more than 40 years ago. There are a class of effects belonging to the photo-galvanic effect (PGE), including the circular PGE (CPGE), the linear PGE (LPGE) and the photon drag effect (PDE). The CPGE refers to the phenomenon that the photocurrent changes sign when the helicity of light changes from left-circularly polarized to right-circularly polarized. It arises from the transfer of the photon angular momentum to excited electrons. Whereas, for the LPGE, the photocurrent is insensitive to the helicity of light. The photon drag effect, differing from the CPGE and LPGE, transfers photon momentum to electrons as well.

The PGEs have been extensively studied in semiconductor quantum wells [51,52] where the inversion symmetry is broken. The CPGE serves as a powerful tool to study the spin splitting of the electronic structures, the symmetry of the crystal and even the relaxation dynamics of the excited electrons. Thus, we expect the CPGE can be used to study the Dirac surface states of 3D TIs, just like the spin-split states in quantum wells. One important prerequisite for CPGE is the inversion symmetry.
breaking. The 3D TI - Bi₂Se₃ family- have rhombohedral crystal structures with space group $D_{3d}^5$. The inversion symmetry is preserved in the bulk, however, at the surface, the inversion symmetry is broken. Therefore, using CPGE to study the surface states has the advantage of no bulk mixing. The transport measurement of the 3D TI is usually impeded by the bulk conduction, but it is not a problem for the CPGE measurement. Fig. 1.15 shows the photocurrent measurement in Bi₂Se₃ that reports the polarization dependent photocurrent.

Figure 1.15. Polarization dependent photocurrent in Bi₂Se₃ (a) Schematic of the photocurrent generation in Bi₂Se₃ thin films with circularly polarized light (b) The photocurrent variation with the polarization of light. Figure reproduced from ref [11].

1.5 Outline

In this dissertation, I shall discuss using optoelectronic methods to study the spin-polarized surface states in 3D topological insulators and the spin pumping at the interface of topological insulator-magnetic insulator heterostructures by light illumination. For each topic, the chemical potential tuning is utilized to split the surface states from the bulk states and sheds light on the underlying physics of the photocurrent generation. Chapter 2 will describe various experimental techniques for different stages of work, from sample synthesis, device fabrication, electrostatic gating to photocurrent measurements. Chapter 3 will start with a brief introduction of previous photocurrent measurements in 3D TIs and what is still a mystery. Then I will proceed to describe the polarization dependent photocurrent
in various (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin films and the analysis of the photocurrent, especially differentiating the CPGE from the PDE by an incidence angle dependence study. I will also describe the dependence of the photocurrent on the chemical potential of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$. The theoretical analysis and numerical calculation conducted by our colleagues are also reported. The comparison between the theory and the experiment is the critical part of this chapter. Chapter 4 will describe the spin pumping induced by light illumination at the interfaces of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ - YIG heterostructures. I shall demonstrate that the light illumination provides a novel way for spin pumping and a spin dependent photocurrent is observed consequently. I will also discuss the origin of the spin dependent photocurrent in this chapter. At the end of each chapter, I will give a short discussion of unresolved problems and directions for future work.
Chapter 2  
Experimental Methods

The work presented in the dissertation involved using optoelectronic methods to study 3D topological insulator (TI) thin films or TIs combined with magnetism. This chapter will address the experimental methods consisting of the fabrication of devices, electrostatic gating with magneto-transport, low noise photocurrent measurements and magneto-optical Kerr microscopy for measurements of magnetization. The fabrication of devices included the epitaxial growth of the topological insulator thin films and the fabrication of the Hall bar structure with the top gate. Since the topological surface states played critical roles, the electrostatic gating was utilized for tuning the chemical potential. The photocurrent measurement, which was the critical part of our study, used noise reduction techniques for detecting a pica-amp level photocurrent. For study of the spin dependent photocurrent in TIs combined with magnetism, we used magneto-optical Kerr microscopy of the magnetization in these systems. These methods will be introduced one by one.

2.1 Device fabrication

2.1.1 Sample growth by molecular beam epitaxy

Molecular beam epitaxy (MBE) is widely used to grow high quality single crystalline thin films with very good control of thickness and stoichiometry. The schematic of a typical MBE system is shown in Fig. 2.1. Though this technique was initially developed for the growth of III-V semiconductors, it has demonstrated the success in growing other various materials, including bismuth chalcogenides. As suggested by its name, the essential idea of MBE is to employ beams of evaporated atoms generated by the effusion cells, and form layers of molecules at surfaces of heated
substrates. One prerequisite for this process is the nearly free movement of the evaporated atoms, which is made possible by the ultra-high vacuum (UHV) of the MBE chamber. Compared to other growth techniques, MBE is featured by the low growth rate ($\sim 1$ ML/s), which enables the precise control over the thickness and the film composition. Another advantage of MBE growth is the in-situ monitor of the thin film quality by a surface sensitive technique, reflection high energy electron diffraction (RHEED). In this dissertation, the 3D topological insulators -Bi chalcogenides thin films - were grown by MBE on various substrates in collaboration with Dr. Anthony Richardella and James Kally.

Figure 2.1. Schematic of a typical molecular beam epitaxy system. Figure from Wikipedia.

Our MBE system has two inner-connected chambers, one (Applied EPI/Veeco 620) for the growth of II-VI semiconductors and the other (Applied EPI/Veeco 920) is dedicated to III-V semiconductors. In the growth of bismuth chalcogenide thin films, we usually used the second chamber for the substrate preparation before the growth and the aluminum capping after the growth. The major growth took place in the first chamber. Sample transfer between chambers were under vacuum. The major growth in MBE was thermally evaporating constituent elements of the thin films from standard Knudsen cells to the heated substrates. By controlling the shutter of each effusion cell, we could control the exposure time of the substrate to each element. Specifically, for bismuth selenide or telluride, the substrate was
exposed to Se or Te for tens of seconds to help the film stick and then exposed to both for certain amount of time depending on how thick films we wanted to grow. The temperature of each effusion cell was precisely controlled for reaching the right composition. Another essential parameter during the growth is the substrate temperature, which varies between substrates for the same thin film. Post-annealing in the Se or Te atmosphere was sometimes found helpful to improve the thin film quality or compensating Se or Te vacancies present in the film. For our experiments, in order to set the chemical potential in the band gap, antimony was doped into the bismuth telluride thin film, which was realized by utilizing the Sb cell in the MBE system. The Bi/Sb ratio is critical for tuning the chemical potential of the thin film, and thus one of the biggest challenges in the growth. We found that doping 50% of Sb to replace the Bi could yield a TI thin film with a low carrier concentration.

2.1.2 Photo-lithography and etching

For the purpose of measuring the photocurrent and magneto-transport in TI thin films, we patterned thin films into Hall bars. One way is to use lithography combined with etching. The lithography process can be categorized into two groups, photo-lithography and e-beam lithography. The general idea of the two methods is the same. Coating thin films with either photo-resist or e-beam resist, and under the effect of UV light or electron-beam, the resist became soluble (positive resist) or insoluble (negative resist) to specific developers. To create patterns, photo-lithography uses masks to create shadows on resist, while e-beam lithography directly uses focused electron beam to scan across the patterns. Because of the diffraction limit of light, photo-lithography cannot pattern a feature less than 1-2 microns. However, due to the significantly smaller wavelength of the electron beam, e-beam lithography can handle sub-micron patterns. Since the effect we studied does not require a very small (sub-micron) device, most of the time, we used photo-lithography to make patterns. The patterning consisted of three steps, spin-coating of a positive photo-resist, aligning the sample with respect to a mask then exposing to UV light and dissolving the exposed photo-resist with developers. The positive photo-resists we used regularly were SPR3000 series and S1800 series.

The next step of device fabrication following lithography is etching. There
are two ways of etching, wet-etching and plasma etching. Wet etching uses liquid chemicals to remove materials. Specifically, for bismuth chalcogenides, we used a mixture of 0.1g potassium dichromate, 25g DI water and 7mL hydrobromic acid. The etching rate was dependent on the substrate of the TI thin film. The wet etching was very rapid (10 nm/s) on substrates like sapphire and YIG, but much slower (<1 nm/s) on InP substrates. The concentration of the potassium dichromate and hydrobromic acid in the mixture can be adjusted accordingly for reasonable etch rates on various substrates. The other way of etching is to use Ar and Cl\textsubscript{2} plasma. In the etching process, physical etching (high energetic bombardment) and chemical etching (chemical reaction with the material) take place simultaneously. Compared to the wet-etch, the resolution of the dry etch is higher, however, it is harder to remove the photo-resist after the plasma etching. If deposition of other materials on top of the TI thin film is needed after the Hall bar patternning, we prefer wet-etch for an easy removal of the photo-resist after etching. The last step of the photo-lithography is to remove the photoresist on top of the Hall bar. The process is usually called "stripping". An illustration of the entire process of the photolithography is shown in Fig. 2.2.

![Illustration of the photo-lithography process](image)

**Figure 2.2. Illustration of the photo-lithography process.** Figure reproduced from the module of Rice University course CHEM-496.
Another method of patterning a Hall bar is mechanical scratching. The scratching system is composed of an optical microscope and a needle for scratching mounted on a two-way automated stage. We can define the pattern by giving all the coordinates of the break points of the pattern. A Labview program can utilize the pattern file and control the stage of the needle. The needle moved around and scratched away the part surrounding the desired pattern. This technique is not as precisely controlled as the photo-lithography, so the pattern after scratch is not as sharp. However, the advantage of this process is water-free, which is extremely helpful to preserve the sensitive surfaces of topological insulator thin films. This technique has restrictions as well. It can not be applied to a material that is hard or a material on a substrate that is soft. For TI thin films grown on sapphire or YIG, we used mechanical scratching for Hall bar patterning if a top gate was not needed.

2.1.3 Fabrication of the top gate

For the purpose of tuning the chemical potential, one way is to fabricate a top gate composed of a dielectric oxide and a conducting gate electrode. Our work is associated with optical methods, so a transparent top gate is a must. Aluminum oxide is a good candidate for the dielectric layer while indium tin oxide is good for the top gate electrode. First of all, both have a transmission near a hundred percent in the visible light range, so light can pass without much loss. Second, aluminum oxide is a high dielectric constant oxide, which can provide efficient chemical potential tuning while indium tin oxide is a good electrical conductor. Third, both aluminum oxide and indium tin oxide are easy to grow. For aluminum oxide, atomic layer deposition is a mature technique for the growth. For indium tin oxide, sputtering at elevated substrate temperatures is one of the easiest growth techniques.

Atomic layer deposition

Atomic layer deposition (ALD) is capable of depositing thin films using gaseous precursors. This technique, differing from the chemical vapor deposition, exposing substrates to alternating pulses of precursors that can react with the surface. The chemical reaction at the surface in each exposure is self-limited and deposits no
more than one monolayer at the surface. After each exposure, the chamber is purged with an inert gas to remove excess precursors and reaction by-products. Because of the self-limiting and sequential nature, ALD has a good control of the thickness and conformity of the deposited thin film. Given sufficient precursor pulse time, the precursor can reach deep trenches and realize a complete reaction with the entire surface.

**Figure 2.3. Illustration of the atomic layer deposition.** One cycle of the atomic layer deposition consists of pulsing and purging of one precursor and pulsing, purging of the other precursor (reactant). The number of cycles determines the thickness of the deposited thin films.

The majority of ALD use two precursors. For aluminum oxide, the two precursors are trimethylaluminium (TMA) and water vapors. As shown in Fig. 2.3, each growth cycle consists of pulse of TMA for 0.03 s, purge for 10 s, pulse of water for 0.1 s and purge for 10 s. The time for each step can be adjusted. In the first half of the cycle, TMA precursors react with the surface and produce -Me (Methyl terminated group) on the Al, then by-products Methane gas and excess TMA are removed during purge. In the second half, with the introduction of water, the ligand exchange between -Me group and -OH group takes place and creates aluminum oxide. This process is then cycled until the desired thickness of oxide
is achieved. Our recipe yields a deposition rate as slow as 0.8 Å/cycle. During the deposition, the substrate was kept at a modest temperature, usually less than 350°C. There is a temperature window for each specific material. If the temperature is too high, thermal decomposition or rapid desorption of precursors can happen; if the temperature is too low, the reaction is too slow and precursors may condense at the substrate. In our case, there is one more restriction on the temperature. We must not heat the TI thin film above 200°C, otherwise, the surface and crystalline of TI films may be damaged. With all the restrictions, we heated the substrate to 110°C in the deposition process of aluminum oxide.

**Sputtering**

Indium tin oxide (ITO) is a ternary composition, which can be treated as a mixture of 90% indium oxide (In$_2$O$_3$) and 10% tin oxide (SnO$_2$). It is one of the most widely used transparent conducting oxides with broad applications in flat-panel displays, polymer-based electronics, thin film photovoltaics, etc. It is a heavily n-doped semiconductor with a large band gap of 3.5 to 4.3 eV. Because of the unique properties, both transparency and conductivity are realized in this material. However, a compromise must be made between conductivity and transparency since increasing the carrier concentration increases the conductivity, but decreases the transparency of ITO. Various deposition techniques have been successfully applied to fabricate ITO thin films including chemical vapor deposition, magnetron sputtering, pulsed laser evaporation, etc. In this work, we used magnetron sputtering for the ITO deposition.

Sputtering is one kind of physical vapor deposition. As shown in Fig. 2.4, target materials are ejected by bombardment with energetic particles, particularly, gas ions. People usually use the inert gas that has a close weight to the sputtered material as the sputtering gas. This guarantees no reaction between the target and the gas ions, as well as an efficient momentum transfer between the gas ions and the target material. Better than evaporation, even materials with very high-melting point can be deposited by sputtering. Additionally, other active gases can be introduced on purpose for chemical reactions with the target material. For example, in the deposition of ITO, oxygen gas is added besides argon gas to compensate oxygen deficiencies in the target ITO.

For the deposition of ITO presented in this dissertation, a Kurt Lesker CMS-18
sputter deposition system was used, as shown in Fig. 2.4(a). The process of sputtering can be generalized as following steps. 1) Substrates were loaded into the high-vacuum chamber and heated to desired temperatures (not always necessary). 2) As a bias was applied between the sputtering target (cathode) and the substrate (anode), the inert gas was introduced into the chamber and got ionized by collisions with stray electrons, thus producing plasma. 3) Once the plasma was generated and sustained, the gas pressure was lowered and the real deposition process started. In the plasma generation step, the gas pressure needs to be high enough to sustain the plasma. We used 40 mTorr of Ar gas to ignite the plasma in the deposition of ITO. However, for the real deposition process, the gas pressure must be lowered to get an efficient deposition rate. Too high a pressure causes too much scattering of the sputtered material on the way to the substrate. Therefore, optimization of the gas pressure is needed for sputter depositions. We used 15 mTorr in the real deposition process of ITO. Besides the gas pressure, another critical factor in the deposition of ITO is the oxygen ratio in the Ar gas. Since the ITO was used for the top gate electrode, the basic requirements were transparency and conductivity. It was found
that increasing the oxygen ratio in the gas could increase the transparency, however, the conductivity of ITO was lowered. In this work, we found 0.05% of oxygen was an appropriate ratio. Substrate temperature and post-deposition annealing are also important for the electrical and optical properties of ITO. However, since the TI film can not stand temperatures above 200°C, we maintained the temperature at 150°C. The conductivity of the ITO grown at 150°C was not as good as 300°C, but the conductivity was sufficiently high for the use as the gate electrode.

2.1.3.1 Lift-off of the gate material

The last two sections described the growth of the dielectric oxide and the conducting electrode. Details of the fabrication process of the gate need to be filled in. The process is as follows: 1) Deposit aluminum oxide by ALD on top of the Hall bar structure of TI thus covering the entire sample. 2) Pattern the window for the top gate electrode by photo-lithography using bi-layer photoresist (LOR 5A + SPR 3012). After developing, a window is opened for the deposition of the ITO layer. 3) Deposit ITO by Sputtering. 4) Lift-off the photoresist by PG-remover in water bath @80°C. The excess ITO on top of the photoresist is removed together with the photoresist. In this process, the use of the bi-layer photoresist is to create an undercut in the pattern since the two photoresists dissolve at different speeds in the developer. With an undercut, the lift-off of the gate material becomes easier. The transmission of the as-grown gate material (Al₂O₃+ITO) is shown in Fig. 2.5. For a wavelength above 550 nm, the transmission is larger than 90%, good enough for this optical study.

![Figure 2.5. Transmission of the gate material.](image)

Transmission in the wavelength range of 450 nm - 1000 nm.
2.2 Tuning the chemical potential with gating

Electrostatic gating can be used to tune the chemical potential without changing the level of disorder. It also provides a far simpler method of exploring the properties of materials than the chemical doping [53]. We present two methods in the dissertation, one is the traditional electrostatic gating with field effect transistor devices, the other is using persistent optical gating on thin films grown on strontium titanate. The latter one was discovered by our collaboration with Prof.Awschalom’s group in University of Chicago. [12]

2.2.1 Electro-static gating with field effect transistors

One common method of electrostatic gating is to construct field effect transistors on semiconductors. The field effect refers to the modulation of the conductivity of a semiconductor by applying an electric field. The change in the conductivity is due to band bending of the conduction and valence bands where the electric field penetrates into. Fig. 2.6 below are schematic pictures of the top gate device and the band bending in a p-type semiconductor as a positive gate voltage was applied. The positive gate voltage depopulated the holes at the surface and would further induce an inversion layer as the gate voltage increases.

![Figure 2.6. Illustration of the top gate device and band bending induced by the gate.](image)

For topological insulator thin films, the field effect transistors can be constructed on top of the TI thin film, or directly use the heterostructure of TI - strontium...
titanate (STO) in TI films grown on STO. In both cases, there is a layer of dielectric with high dielectric constant and a layer of conducting electrode. In our work, we preferred the top gate structure since the light was probing the top surface. In the last section, we already described the fabrication of the top gate using aluminum oxide and indium tin oxide. For 30nm Al$_2$O$_3$ + 300nm ITO, a gate voltage in the range of -15 V to 15 V was usually applied on the top gate device. The leakage current was kept under 0.2 nA to preserve the gate. For (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin films with the initial chemical potential in the gap, the top gate was capable of tuning the chemical potential through the Dirac point.

2.2.2 Persistent optical gating

Another way of gating was discovered through our collaboration with Prof. Awschalom’s group in University of Chicago. TI thin films on STO substrates were grown in our group and sent to University of Chicago where they found an exposure to UV light can change the resistance of the TI thin film. It was discovered that the UV exposure was equivalent to applying a positive gate voltage which tuned the chemical potential up. This optical gating effect was persistent after removing the light. However, a red light can be used to reverse the persistent chemical potential tuning induced by the UV light. Therefore, a bidirectional optical control of the chemical potential of TI thin films were demonstrated. As shown in Fig. 2.7, exposure to light with photon energy larger than the STO band gap raised the chemical potential of the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film, whereas light with energy lower than the band gap brought down the chemical potential. We attributed this gating effect to optically induced electrical polarization in the STO substrate. Fig. 2.8 shows the comparison of the electrical properties of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ between the electrostatic gating and the optical gating. The two gating methods tuned the chemical potential in a similar manner. The discovery of the persistent gating effect was reported in the paper "Persistent optical gating of a topological insulator" published on Science Advances. [12]
2.3 Low-noise photocurrent measurement

The major goal of the thesis is the optoelectronic study of the topological insulators, specifically measuring the photocurrent induced by a polarized light or an external magnetic field. The photocurrent measurement was not trivial since the signal was only a few pAs. Thus, we used noise reduction techniques to help improve the
signal noise ratio in this study. Fig. 2.9 shows a typical set up of the photocurrent measurement.

Figure 2.9. Set-up of the photocurrent measurement. The set-up illustration has included the major components of the photocurrent measurement set-up. Some optical components are skipped here.

The excitation was a He-Ne laser with an intensity of 7.5 mW. The laser beam was modulated by an optical chopper at a frequency of 569 Hz. The laser modulation created an AC signal in the photocurrent measurement, which could filter out noises at other frequencies when using a lock-in amplifier for detection. Before the detection with the lock-in, a current preamplifier was used to amplify the current signal and convert the signal to a voltage. Fig. 2.9 shows the set-up of the measurement with a laser, a chopper, a cryostat where the sample was mounted, a current preamplifier and a lock-in amplifier. Additional optical components that were used to reflect, focus or alter the beam were not shown in this set up. There were a few tips of lowering the current noise. First of all, we chopped the beam and set the lock-in amplifier to the chopping frequency. The phase of the lock-in amplifier was set at the phase of the reflection beam intensity. Secondly, the amplification of the current preamplifier was set to $5 \times 10^6$ V/A for a reasonable input impedance and output voltage. Thirdly, co-axial wires were used inside the cryostat to screen any external fields that may impose on the small current. Last, the grounding
was carefully handled that no current was from the grounding loop. With all the tips, the typical current noise in our system was 0.3 pA to 2 pA when using a time constant of 300 ms on the lock-in setting. The noise level still varied between samples.

2.4 Magneto-optical Kerr microscopy

In this dissertation, we use the magneto-optical Kerr microscopy to measure the magnetization of magnetic materials. Magneto-optical Kerr effect (MOKE) is one kind of magneto-optic effects, which was discovered by the Rev. John Kerr in 1877. MOKE refers to the change to the light’s polarization reflected from a magnetized surface. This effect is similar to the Faraday’s effect, which was discovered in 1845. The only difference is that the Faraday’s effect studies the transmitted light while MOKE studies the reflected light. Today magneto-optic effects are widely applied in research of magnetism.

Magneto-optical Kerr effect arises from the off-diagonal elements in the dielectric tensor. An incident linearly polarized light can be viewed as a combination of the left-circularly polarized light and right-circularly polarized light. Without any external field, the circularly polarized electric field will drive the electrons into circular motions. The radius of the electron’s orbit is the same for left-circular polarization and right-circular polarization. Once a magnetic field is present, an additional Lorentz force acting on the electrons will induce a change in the radii of the electrons’ orbits. The difference in the radii for left-circular polarization and right-circular polarization will yield different dielectric constants. For ferromagnetic materials, an additional effective field is present besides the applied external field. This effective field results from the spin-orbit coupling that the electrons feel in the orbital motions. The coupling between the magnetic moment of the electron with its motion causes the unusual magneto-optic effect of the ferromagnetic materials.

The MOKE measurements have three geometries, polar, longitudinal and transverse. They differ in the direction of the magnetic field with respect to the incidence plane and the sample surface. As shown in Fig. 2.10, (a) refers to the polar MOKE in which the magnetic field is parallel to the plane of incidence while normal to the sample surface; (b) refers to the longitudinal MOKE in which the magnetic field is parallel to both the incidence plane and the sample surface; (c) refers to
the transverse MOKE in which the magnetic field is normal to the incidence plane while parallel to the sample surface. The polar MOKE is most frequently studied with a near-zero incidence angle. For the other two geometries, MOKE can not be observed with normal incidence.

Figure 2.10. Three different geometries of MOKE. (a) Polar MOKE (b) Longitudinal MOKE (c) Transverse MOKE

For the study of the in-plane magnetization, we use longitudinal MOKE. An incident linearly polarized light experiences a rotation of the polarization plane, called Kerr rotation and a phase difference between the p component and s component of the incidence light, referred as Kerr ellipticity. We measure the Kerr rotation by detecting the intensity of the reflected light after passing an analyzer set at 90 degrees off the initial polarization plane. A schematic of the longitudinal MOKE is shown in Fig. 2.11. The laser is optically modulated and the intensity of the reflected light is measured with a photo-diode along with a lock-in amplifier. The AC measurement of MOKE can help improve the sensitivity.
Figure 2.11. Schematic of the longitudinal MOKE
Chapter 3  
Helicity Dependent Photocurrent in Topological Insulators

3.1 Introduction

This chapter is based on the paper submitted to Nature Communications. Bichalcogenides have attracted much contemporary interest as three-dimensional (3D) "topological insulators" (TIs) that host gapless spin-textured surface states which reside within the bulk band gap. The spin-momentum locking in these helical Dirac states provides a unique opportunity for "topological spintronics" devices that function at technologically relevant temperatures (300 K and above). [9,10,54] Optical methods have also been adopted to control electron spin and charge currents in 3D TIs. [55–58] In particular, experiments have shown that circularly polarized light induces a directional helicity-dependent photocurrent (HDPC) in 3D TIs: in other words, light of opposite circular polarization yields a photocurrent propagating in opposite directions. [11] The ready observation of this phenomenon at 300 K promises interesting opportunities for developing opto-spintronic devices wherein electron currents might be steered optically. Progress toward such technological applications is however impeded by a lack of understanding about the physics underlying this phenomenon.

The natural impulse is to immediately attribute the HDPC in 3D TIs to the helical spin texture of the Dirac surface states: [11] circularly polarized photons couple to the spin-momentum locked topological surface states, yielding a circular photo-galvanic effect (CPGE), a phenomenon well-established in semiconductor quantum wells, where the inversion symmetry breaking is the cause. [51,52] Time-resolved measurements of the HDPC in 3D TIs seem to confirm the surface-related
origin for the HDPC by showing that the group velocity of the induced photocurrent matches that expected for Dirac surface electrons. However, this interpretation is difficult to reconcile with the fact that the photon energy used in the experiments is about 5 times larger than the bulk energy gap. This means that the optical transitions involved in creating photo-electrons cannot involve the Dirac surface states alone. In principle, HDPC can also be generated by the photon drag effect which involves the transfer of both spin angular momentum and translational momentum from circularly polarized photons to electrons. It is thus relevant to develop an experimental test that distinguishes between CPGE and photon drag as the origin of the HDPC. Another relevant question is the underlying microscopic mechanism for the HDPC. While both the CPGE and the photon drag effect can be related to optical transitions involving the lowest energy surface states alone, there are several other possibilities. These include the asymmetric scattering of electrons, a “surface shift current", a photocurrent arising from Rashba states, and a photocurrent arising from excitation into the second excited band of surface states. So far, there have been very few attempts to clearly rule out any of these alternative interpretations. Therefore, we develop a systematic study of the helicity dependent photocurrent in thin films of electrically gated 3D TI (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$.

3.2 Polarization dependent photocurrent measurements

3.2.1 Experimental set-up

In the photocurrent measurement, a continuous He-Ne laser (633 nm) was used as the excitation source. The measurement was taken on 10-20 QL thick (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin films, patterning to a 100 µm wide Hall bar. As shown in Fig. 3.1, the samples were illuminated at the center of the Hall bar to eliminate any contribution from the thermo-electric current. In the incoming beam path, a linear polarizer was used to make the laser purely p-polarized, followed by a quarter wave-plate (QWP) to change the polarization of light from linearly polarized to circularly polarized (left or right). To realize the tuning of the polarization, the angle $\varphi$ of the QWP (the angle between the fast axis and p-polarized light) was tuned from 0 degree to 360 degree. Then a 100 mm plano-convex lens was used to focus down the laser to a
100 µm wide beam on the sample surface with an nonzero incidence angle.

Figure 3.1. Experimental set-up of the photocurrent measurement. Schematic of the excitation and measurement of photocurrent with obliquely incident excitation in the x−z plane. A quarter wave-plate is used to tune the polarization of light and the photocurrent is measured along the y-axis.

As light was incident in the x-z plane, we measured the photocurrent along x or y direction, parallel or perpendicular to the excitation plane. Details of the photocurrent measurement was already introduced in the Methods chapter. The Hall bar structure of the sample was utilized to measure the transport properties, four probe longitudinal resistance (R_{xx}) and Hall resistance (R_{xy}), besides the photocurrent measurement. With the transport measurement, the carrier concentration of the sample and the relative position of the chemical potential with respect to the Dirac point were revealed.

### 3.2.2 Extraction of the helicity dependent photocurrent

For the laser incident at 45 degree, we measured the photocurrent as a function of ϕ along the main channel of the Hall bar (y axis) on device A, 20 QL (Bi_{0.52}Sb_{0.48})_2Te_3 thin film. When ϕ was 0°, 90° or 180°, light was p-polarized; when ϕ was 45° or 135°, light was left or right circularly polarized. In Fig. 3.2 shown below, we noted that the photocurrent not only changed as the polarization was varied, but
also reversed sign as the helicity of the light reversed from left-circular polarized to right-circular polarized. We also found that we could fit the polarization dependent photocurrent with this expression,

\[ I(\varphi) = C \sin(2\varphi) + L_1 \sin(4\varphi) + L_2 \cos(4\varphi) + D \]  

(3.1)

where the first term \( C \sin(2\varphi) \) described the contribution from circularly polarized light, the helicity dependent photocurrent (HDPC), the second and third terms, \( L_1 \sin(4\varphi) \) and \( L_2 \cos(4\varphi) \), denoted the contributions from linearly polarized light and the last term \( D \) identified an offset photocurrent independent of the polarization.

The fit to this equation (solid line in Fig. 3.2(a)) agreed well with the experimental data. We also obtained the magnitudes of \( C \), \( L_1 \), \( L_2 \) and \( D \) from the fits (Fig. 3.2(b)). The offset \( D \) was mainly contributed by a dark current which we could not eliminate without laser. The linear polarization dependent photocurrents \( L_1 \sin(4\varphi) \) and \( L_2 \cos(4\varphi) \) were not major components in the photocurrent we observed.

Several experiments focusing on the linear polarization generated photocurrent in topological insulators found its origin from the photon drag effect [69]. Apart from \( D \), \( L_1 \) and \( L_2 \), the HDPC identified by \( C \), dominated the polarization dependent photocurrent. The amplitude of \( C \) was about 11 pA.

### 3.2.3 Physical mechanism of the helicity dependent photocurrent

Up to second order in the laser electric field, the HDPC can be attributed to two principal mechanisms, namely the CPGE and the circular photon drag effect (CPDE). [60, 61, 70] Macroscopically, the CPGE is described by the expression \( I_j = \gamma_{js}(ie \times e^*)_sJ \) and the CPDE is given by \( I_j = \tilde{T}_{jks}q_k(ie \times e^*)_sJ \), where \( j, k, s = x, y, z \) and \( e, q \) and \( J \) denote the unit vector of the electric field, the momentum of the incident light and its intensity, respectively. The term \( (ie \times e^*) \) identifies the helicity of the light, which varies from \(-1\) to \(+1\) and is zero for linearly polarized light. The non-zero components of the tensors \( \gamma \) and \( \tilde{T} \) are restricted by the crystal symmetry.

For the bulk of \((\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3\), \( \gamma \) is zero because of inversion symmetry. However, the surface has a reduced symmetry of \( C_{3v} \), corresponding to a three-fold rotation symmetry around z axis and three mirror planes in the x-y plane. For CPGE,
Figure 3.2. Room temperature polarization dependent photocurrent (a) Room temperature photocurrent along the y-axis in device A. At $\varphi = 45^\circ$, the laser is left circularly polarized and the photocurrent is negative. At $\varphi = 135^\circ$, the laser is right circularly polarized and the photocurrent is positive. The solid line is a fit to Eq. 3.1. (b) The coefficients $C$, $L_1$, $L_2$, $D$ as extracted from the fit in (a). The amplitude $C$ of the HDPC dominates the polarization dependent photocurrent.

under a rotation of $\frac{2\pi}{3}$, $\hat{e} \times \hat{e}^*$ becomes $R(\hat{e} \times \hat{e}^*)$. $R$ is the rotation matrix and equals to
\[
\begin{pmatrix}
\cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) & 0 \\
-sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]
$I$ becomes $RI$. Because of the rotational symmetry, the tensor $\gamma$ should remain the same. Therefore, we obtain that $RI = i\gamma R(\hat{e} \times \hat{e}^*) J$. After replacing $I$ with $i\gamma (\hat{e} \times \hat{e}^*) J$, we deduce that $R\gamma = \gamma R$. To satisfy this relation, $\gamma$ must have a form of
\[
\begin{pmatrix}
\gamma_{xx} & \gamma_{xy} & 0 \\
-\gamma_{xy} & \gamma_{xx} & 0 \\
0 & 0 & \gamma_{zz}
\end{pmatrix}.
\]
Furthermore, the mirror symmetry imposes an additional constraint on the form of $\gamma$. There are three mirror planes, and the angle between the mirror plane and the x axis is defined as $\phi$. Under the mirror reflection, $I$ becomes $MI$; however, as a pseudo-vector, $\hat{e} \times \hat{e}^*$ becomes $-M(\hat{e} \times \hat{e}^*)$. $M$ equals to
\[
\begin{pmatrix}
\cos(2\phi) & \sin(2\phi) & 0 \\
\sin(2\phi) & -\cos(2\phi) & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]
Therefore, $M\gamma = -\gamma M$. Combining the two constraints from the mirror symmetry and
Thus, we conclude that \( \gamma \) must have a form of 
\[
\begin{pmatrix}
0 & \gamma_{xy} & 0 \\
-\gamma_{xy} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]

Thus, 
\[
I = iJ \begin{pmatrix}
\gamma_{xy}(\hat{e} \times \hat{e}^*)_y \\
-\gamma_{xy}(\hat{e} \times \hat{e}^*)_x \\
0
\end{pmatrix}.
\]

For CPDE, the photocurrent is expressed as 
\( I_j = \hat{T}_{jk}q_k(ie \times e^*)_sJ \). We define vector \( \hat{h} \equiv \hat{e} \times \hat{e}^* \). For a transverse electromagnetic wave, the vector \( \hat{h} \) should along the same direction as the photon’s momentum \( \hat{q} \). Therefore, 
\[
q_i h_j = q_j h_i.
\]
We can define \( \hat{e}_{ij} \equiv \hat{T}_{ij} = \hat{T}_{ijx} + \hat{T}_{ijy} + \hat{T}_{ijz} \). Under the rotation of \( \frac{2\pi}{3} \), 
\[
I' = RI = \begin{pmatrix}
R_{xx} \hat{T}_{ijx} + R_{xy} \hat{T}_{ijy} \\
R_{yx} \hat{T}_{ijx} + R_{yy} \hat{T}_{ijy} \\
\hat{T}_{ijz}
\end{pmatrix} q_i h_j.
\]
On the other hand, 
\[
I' = iJ \begin{pmatrix}
\hat{T}_{ijx} M_{ik} q_k R_{js} h_s \\
\hat{T}_{ijy} M_{ik} q_k R_{js} h_s \\
\hat{T}_{ijz} M_{ik} q_k R_{js} h_s
\end{pmatrix}.
\]
For \( I'_z \), we get 
\[
\hat{T}_{zij} q_i h_j = \hat{T}_{zij} R_{ik} q_k R_{js} h_s.
\]
Each term \( q_i h_j \) needs to be equalized. Therefore, these conditions that \( \hat{T}_{z3} = \hat{T}_{z5} = \hat{T}_{z2} = 0 \) and \( \hat{T}_{z4} = \hat{T}_{z1} \) need to be satisfied. Combined with the restrictions we get from \( I'_x \) and \( I'_y \), we conclude that \( \hat{T}_{x1}, \hat{T}_{x2}, \hat{T}_{x3}, \hat{T}_{x5}, \hat{T}_{z1} \) and \( \hat{T}_{z6} \) are independent variables while \( \hat{T}_{x6} = \hat{T}_{x2} = \hat{T}_{z3} = \hat{T}_{z5} = 0 \), \( \hat{T}_{x1} = -\hat{T}_{x1}, \hat{T}_{y1} = \sqrt{3} \hat{T}_{x1}, \hat{T}_{y2} = -2\hat{T}_{x1}, \hat{T}_{y3} = -\hat{T}_{z5}, \hat{T}_{y4} = -\frac{1}{2} \hat{T}_{x2}, \hat{T}_{y5} = \hat{T}_{x3} \) and \( \hat{T}_{z4} = \hat{T}_{z1} \). Besides, \( \hat{T} \) needs to satisfy mirror symmetry. Thus, 
\[
\begin{pmatrix}
M_{xx} \hat{T}_{ijx} + M_{xy} \hat{T}_{ijy} \\
M_{yx} \hat{T}_{ijx} + M_{yy} \hat{T}_{ijy} \\
\hat{T}_{ijz}
\end{pmatrix} q_i h_j = \begin{pmatrix}
\hat{T}_{ijx} M_{ik} q_k (-M_{js} h_s) \\
\hat{T}_{ijy} M_{ik} q_k (-M_{js} h_s) \\
\hat{T}_{ijz} M_{ik} q_k (-M_{js} h_s)
\end{pmatrix}.
\]
Additional constraints on \( \hat{T} \) can be derived by matching each \( q_i h_j \) term. Eventually we find that only 
\[
\hat{T}_{y3} = -\hat{T}_{x5} = \kappa \text{ are nonzero. Therefore, } I = iJ \begin{pmatrix}
-\kappa q_z (\hat{e} \times \hat{e}^*)_y \\
\kappa q_z (\hat{e} \times \hat{e}^*)_x \\
0
\end{pmatrix}.
\]

For a monochromatic light shed in the x-z plane, \((\hat{e} \times \hat{e}^*)_y = 0\). Therefore, the photocurrent only flows along y direction for both CPGE and CPDE. Moreover, for an incidence angle of \( \theta \), \( i(\hat{e} \times \hat{e}^*)_x = P \sin \theta \) and \( q_z = -q \cos \theta \), where \( P \) stands for the helicity of the light. Therefore, 
\[
J_{\text{CPGE}} = -\gamma_{xy} P \sin \theta J \text{ and } J_{\text{CPDE}} = -\kappa P q \sin \theta \cos \theta J.
\]
Taking into account that \( P = \sin (2\varphi) \), where \( \varphi \) denotes the angle between the fast axis of the quarter wave plate and the initial linear polarization of the light, we conclude that 
\[
J_{\text{CPGE}} \propto \sin (2\varphi) \sin (\theta) \text{ and } J_{\text{CPDE}} \propto \sin (2\varphi) \sin (2\theta).
\]
Though both effects have the same $\varphi$ dependence and contribute to the coefficient $C$ in Eq. (3.1), they can be differentiated through their distinct dependences on the incident angle $\theta$. Fig. 3.3 shows a linear dependence of the coefficient $C$ with respect to $\sin \theta$, thus confirming the CPGE as the physical mechanism of the HDPC and ruling out any observable contributions from CPDE.

3.2.4 The directionality of the helicity dependent photocurrent

For circular photo-galvanic effect in Bi-chalcogenides under the surface symmetry of $C_{3v}$, the direction of the HDPC should be perpendicular to the incidence plane, as argued in the previous section. Here we demonstrated the directionality of the HDPC by measuring the photocurrent along different directions on device B with two identical conduction channels along x and y axis respectively. The laser was shed in the x-z plane with an oblique incidence angle of 33°. The Fig. 3.4 shows the polarization dependent photocurrent along each channel with fittings to Eq. 3.1 denoted by solid curves. We found that the HDPC amplitude $C$ was about 4 pA along y axis and was lower than 0.1 pA along x axis. This directionality was consistent with the symmetry argument of the CPGE. Though we didn’t study the
origin of the linear polarization dependent photocurrent, we noted that $L_1$ and $L_2$ from the fitting to 3.1 had different dependences on the directions, implying different origins between $L_1$ and $L_2$, which was consistent with the previous study. [11]

$$I_{\text{photo}} = C\sin(2\phi) + L_1\sin(4\phi) + L_2\cos(4\phi) + D$$

Figure 3.4. The directionality of the helicity dependent photocurrent (a) The polarization dependent photocurrent in device B. Red and blue scatters denote the photocurrent along each conduction channel and are both fitted to Eq. 3.1 of the main text, denoted by the solid lines. (b) We extracted $C$, $L_1$ and $L_2$ from the Eq. 3.1 along x axis (blue) and y axis (red).

The other directional property of CPGE is related to the crystal direction on the (0001) surface of the Bi-chalcogenides. Under the $C_{3v}$ symmetry of the surface, the photocurrent induced by CPGE should be the same along any crystal direction. We provided an evidence of this directionality by measuring photocurrent on device C with four conducting channels along different crystal directions (shown in Fig. 3.5(a)). Since the angle between every adjacent two channels is 45 degree, we labeled the channels as 0 deg, 45 deg, 90 deg and 135 deg by the relative angles. The laser was shed in the x-z plane and we measured the photocurrent along each channel after rotating the device and aligning the measured channel along y axis. We plotted the polarization dependent photocurrent along each channel in Fig. 3.5(b) and found little difference between photocurrents along different channels. The variation of the HDPC was less than 10%. This result demonstrated that the HDPC did not vary with the crystal direction along which the photocurrent was measured. It was therefore confirmed that the HDPC originated from the CPGE. In addition, we could rule out the contribution from the surface shift current since the HDPC had a higher order of symmetry than the three-fold rotational
symmetry. [64,71]

![Figure 3.5](image)

**Figure 3.5. Azimuthal angle dependence of the helicity dependent photocurrent** (a) The schematic of the device C, which consists of four conduction channels along different crystal directions. They are noted by the relative angle of the channel direction. The photocurrent along each channel is measured after reorienting the channel along y axis. (b) The polarization dependent photocurrent along each channel. They are fitted to Eq. 3.1 and the extracted HDPC varies less than 10%.

### 3.3 Study of the helicity dependent photocurrent with a top gate

#### 3.3.1 Transport properties of the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film

We measured four probe longitudinal resistance ($R_{xx}$) and Hall resistance ($R_{xy}$) on device D, 100µm wide Hall bar on 10 QL (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film with top gate (30µm Al$_2$O$_3$ and conducting electrode, indium tin oxide). The fabrication details of the heterostructure were described in Methods chapter. As the sample was cooled down, $R_{xx}$ versus temperature was measured and shown in Fig. 3.6(a). $R_{xx}$ increased monotonically with decreasing temperature, and this insulating behavior identified the chemical potential locating in the band gap.

At 15K, the gate voltage dependences of $R_{xx}$ and $R_{xy}$ were reported, as shown in Fig. 3.6(b). $R_{xx}$ reached a peak near 0 V, indicating the chemical potential passing
the Dirac point. The total change of $R_{xx}$ corresponded to the chemical potential movement inside the band gap. However, we noted that $R_{xy}/B$ never changed sign in the sweeping voltage range as expected. This was due to additional carrier doping in the seed layer (1-2 nm of Bi$_2$Se$_3$) at the interface with the substrate. The additional carrier doping induced the shift of $R_{xy}$, but we could still see the rapid change of $R_{xy}/B$ in the voltage region when $R_{xx}$ reached the peak, indicating the carrier type change in the top layer. In sum, the resistance measurements helped us identify the chemical potential position with respect to the Dirac point.

Figure 3.6. Four probe resistance at low temperatures (a) Temperature dependence of four probe longitudinal resistance; $R_{xx}$ shows an insulating behavior. (b) Longitudinal resistance ($R_{xx}$) and the slope of Hall resistance with respect to out of plane magnetic field ($R_{xy}/B$) versus the top gate voltage. The carrier type changes from n to p type at a voltage near 0V.

3.3.2 Gate voltage dependence of the helicity dependent photocurrent

We next explored how the HDPC depended on the gate voltage, with the aim of elucidating the microscopic origin of the HDPC and the role (if any) of the topological surface states. The photocurrent measurement was carried out in a similar configuration as discussed above (Fig. 3.1), with a fixed incidence angle of $33^\circ$. Fig. 3.7(a) shows the Hall bar structure of this device under the microscope. Fig. 3.7(b) shows the photocurrent as a function of $\varphi$ for different gate voltages, along with fits to Eq. (3.1), shown by the solid lines. (The photocurrent at different
gate voltages is offset on the y-axis for clarity.)

Figure 3.7. Helicity dependent photocurrent in the top gated (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$

(a) Picture of the top gate device under the microscope, different parts are labeled.
(b) The polarization-dependent photocurrent at different $V_{GT}$ is measured at 15 K in
device D. The photocurrents are offset for a better display. We fit the polarization
dependent photocurrent at each $V_{GT}$ to Eq. 3.1, denoted by the solid line. (c) Four probe
measurement of the longitudinal resistance $R_{xx}$ as a function of the gate voltage, denoted
by the red curve. The absolute value $|C|$ of the amplitude of the HDPC is denoted by
the blue curve.

The gate voltage dependence of the HDPC, characterized by the coefficient $C$,
is shown by the blue line in Fig. 3.7(c). The longitudinal resistance is also shown
in the plot as a reference to the chemical potential tuning by the electrostatic
gating (red line). We noted two interesting features in this plot. First, both the

47
HDPC and $R_{xx}$ reached a maximum at the same gate voltage, when the chemical potential for electrons reached the Dirac point. Second, the gate voltage dependence of the HDPC was asymmetric: it decreased faster with a positive gate voltage when the chemical potential was tuned toward the conduction band edge. These characteristics appeared to be generic and were reproduced in device E (10 QL (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film) and device F (10 QL (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film), which were fabricated under similar conditions but with lower Sb concentrations (Fig. 3.8). Therefore, the observation that the HDPC maximizes when the chemical potential crosses the Dirac point, is repeatable and intrinsic for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin films and independent of initial carrier concentrations, sample qualities, as well as other material details.

![Figure 3.8](image)

**Figure 3.8. Helicity dependent photocurrent in various Sb doped (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin films.** From the device D to F, we dope less Sb into Bi$_2$Te$_3$. (a) The gate voltage dependence of the longitudinal resistance $R_{xx}$. The magnitude of $R_{xx}$ in device F (blue curve), taken by a two probe measurement, is much larger than $R_{xx}$ in devices D and E, taken by four probe measurements. Thus, we plot the $R_{xx}$ of device F under a different scale on the right axis of the figure. The different peak positions of $R_{xx}$ in devices D, E and F correspond to the Dirac points of D, E and F, respectively. (b) The gate voltage dependence of the absolute value of the HDPC amplitude– $|C|$.  

### 3.3.3 Wavelength dependence of the helicity dependent photocurrent

Additional insights into the HDPC were gained by varying the wavelength of the optical excitation. Fig. 3.9(a) shows the photocurrent in device D as a function of
polarization for several optical excitation wavelengths between 704 nm and 1000 nm, at a fixed excitation intensity. We extracted the coefficient $C$ by fitting the data to Eq. (3.1). Fig. 3.9(b) shows the gate voltage dependence of $C$ for different wavelengths, revealing a systematic pattern wherein the HDPC reversed sign as the wavelength was increased from 704 nm (photon energy of 1.76 eV) to 1000 nm (photon energy of 1.24 eV). Note that at the extreme ends of the wavelengths studied (704 nm and 1000 nm), the magnitude of the HDPC still reached a maximum close to zero gate voltage (i.e. when the chemical potential is at the Dirac point). At an intermediate wavelength, 820 nm (photon energy of 1.51 eV), the HDPC at zero gate voltage was close to zero and varied monotonically with the gate voltage without revealing any peak. The complex behavior of the HDPC when varying the gate voltage and light wavelength cannot be explained by a simple picture and requires a sophisticated theoretical model which we develop later.

3.3.4 Photocurrent from the bottom surface illumination

We also measured the photocurrent from the bottom surface of $(\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3$ in device D by flipping the sample upside down. Because of the transparency under a visible light, the 633nm laser could penetrate through the sapphire substrate. We compared the polarization dependent photocurrent with the illumination on the bottom surface (red curve) in Fig. 3.10(a) to the photocurrent with the illumination on the top surface (blue curve). The polarization dependent photocurrent induced by the two surfaces’ illumination were much alike. Further, we studied the gate voltage dependence of the HDPC. Since the thin film was 10 QL thick, the electric field created by the top gate was not fully screened at the bottom surface. Fig. 3.10(b) showed that the HDPC from the bottom surface illumination was still tunable by the top gate. However, the peak magnitude of the HDPC was smaller and a larger gate voltage was needed to tune the HDPC to the maximum. The difference in the gate voltage dependence of the HDPC from the top and bottom surface illumination demonstrated the surface origin of the helicity dependent photocurrent.

49
Figure 3.9. Photocurrent excited by photons of different wavelength, ranging from 704 nm (1.76eV) to 1000 nm (1.24eV). (a) The polarization-dependent photocurrent at each wavelength, with solid lines showing fits to Eq. 3.1. The curves are vertically offset for clarity. (b) The gate voltage dependence of the HDPC at five different photon energies ranging from 1.24 eV to 1.76 eV. At 1.24 eV, the HDPC is positive and reaches a peak at the voltage corresponding to the Dirac point in the $R_{xx}$ measurement. When we increase the photon energy, the HDPC starts to become negative and finally becomes a valley at 1.76 eV. The valley bottom is also around the Dirac point.

3.4 Theoretical analysis of the helicity dependent photocurrent

Since CPGE can only arise in the presence of broken inversion symmetry and the bulk crystal structure of tetradymite Bi-chalcogenides is inversion symmetric, previous studies of HDPC in 3D TIs had attributed its origin to topological surface states. [72, 73] However, such interpretations had yet to explain experimental observations rigorously. For instance, the photon energies used in past experiments probing HDPC in 3D TIs were in the range $1 - 2$ eV, well above the bulk band gap where the surface states are located. Thus, the optical excitation could not
The polarization dependent photocurrent induced by the illumination on the bottom surface, as compared to the top surface illumination induced photocurrent. The solid curves denoted the fittings to Eq. 3.1. (b) Gate voltage dependent HDPC for both top and bottom illuminations. The HDPC from the bottom surface was not as tunable as the top surface because of the partially screened gating effect at the bottom surface.

simply involve transitions between spin-momentum locked surface states alone; the relevant optical transitions must involve both topological surface states and bulk states. In this case, it is not clear how circularly polarized photons can excite charge carriers with a preferred spin and momentum.

3.4.1 First principles calculation of the band structure of (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$

We approached the problem of calculating the photocurrent by starting with a first principles calculation of the band structure in (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$, as shown in Fig. 3.11. Since surface states were located inside the bulk band gap around zero energy in Fig. 3.11, we focused on bulk states in the energy range of $\pm 1$ eV~$\pm 2$ eV around the bulk gap (denoted by the blue shaded area), which were described by $\Gamma^\pm_6$ or $\Gamma^\pm_{4,5}$ representations. Then, we considered the contribution to the photocurrent from different bulk states, separately. First, we focused on the $\Gamma^\pm_6$ bulk bands which provided the dominant contribution in the energy range of the photons.
Figure 3.11. First principles calculation of the bulk band structure of (Bi\textsubscript{0.5}Sb\textsubscript{0.5})\textsubscript{2}Te\textsubscript{3}. The irreducible representation to which each bulk band belongs is marked on top of the band. The blue shaded area identifies the energy range which is ±1 – ±2 eV away from the surface Dirac cone, relevant for optical transitions at the photon energy we use.

3.4.2 Optical transitions between the surface states and the bulk states

Based on Fermi’s golden rule, the general expression of photocurrent induced by optical transitions [73–75] between the surface states and the bulk states is derived as

$$J = -\frac{2ne}{\hbar} \sum_{\mathbf{k},(\eta,\xi)} \left( \tau_{pb} \mathbf{v}_{b,\mathbf{k},\eta} - \tau_{ps} \mathbf{v}_{s,\mathbf{k},\xi} \right) \left| \langle \phi_{b,\mathbf{k},\eta} | H_{int} | \phi_{s,\mathbf{k},\xi} \rangle \right|^2 \left( f^0_{s,\mathbf{k},\xi} - f^0_{b,\mathbf{k},\eta} \right) \frac{\delta(E_{b,\mathbf{k},\eta} - E_{s,\mathbf{k},\xi} - \hbar\omega)}{2},$$

(3.2)

where $\tau_{pb}$, $\tau_{ps}$ represents the relaxation time of excited carriers in the bulk band and in the surface states, respectively; $H_{int}$ describes the interaction between electrons and light, $\phi_{b,\mathbf{k},\eta}$ and $E_{b,\mathbf{k},\eta}$ are the eigen-wavefunction and eigen-energy for bulk states with band index $b$ and spin index $\eta$, and $\phi_{s,\mathbf{k},\xi}$ and $E_{s,\mathbf{k},\xi}$ are for topological surface state with the index $\xi$ labelling upper and lower Dirac cones. $\mathbf{v}_{b,\mathbf{k},\eta}$ and $\mathbf{v}_{s,\mathbf{k},\xi}$ are the velocity of bulk and surface bands while $f^0_{b,\mathbf{k},\eta}$ and $f^0_{s,\mathbf{k},\xi}$ are the
corresponding equilibrium Fermi distribution functions.

Equation (3.2) can be evaluated numerically to obtain the photocurrent for photons with a certain helicity, but we first analyze the structure of this expression to identify the requirement for a non-zero photocurrent. The velocity operator \(v_{b(\xi),k,\eta(\xi)}\) in Eq. (3.2) is odd in \(k\), and thus, only asymmetric terms of the transition matrix element \(|M_{\eta\xi}|^2 = |\langle \phi_{b,k,\eta} | H_{int} | \phi_{s,k,\xi} \rangle|^2\) with respect to \(k\) contribute to a non-zero photocurrent. The light-matter interaction \(H_{int}\) in the matrix element is derived from the minimal coupling \((k \rightarrow \Pi = k - \frac{e}{\hbar} A)\) as \(-\frac{e}{\hbar} A \cdot \hat{p}\) and approximated to \(-\frac{e}{m} A \cdot \hat{p}\) for a \(k \cdot p\) Hamiltonian in the small momentum \(k\) limit. For the optics setup shown in Fig. 3.1, the vector potential of the light can be expressed as \(A(t) = A_E e^{-i\omega t + i\alpha r}(-\cos(\theta)(1-\cos(2\varphi)), -\sin(2\varphi), -\sin(\theta)(1-\cos(2\varphi))) + \text{c.c.}\), where \(\varphi = \pi/4, 3\pi/4\) corresponds to left, right circularly polarized light, respectively. The asymmetric part of the corresponding matrix element is given by \(|M_{\xi}|^2_a = \zeta_b \Delta \xi \sin(2\varphi) \sin(\theta) \sin(\theta_k)\), where the subscript \(a\) labels the asymmetric part, \(\theta_k\) identifies the angle of the momentum \(k\) with respective to the \(k_x\) direction, \(\zeta_b = +\) for valence bands and \(\zeta_b = -\) for conduction bands, the parameter \(\Delta\) depend on the bulk index \(b\) and we sum over spin index \(\eta\) of bulk bands because of the spin degeneracy. Thus, the generated photocurrent is proportional to \(\sin(2\varphi) \sin(\theta)\), corresponding to the HDPC. For optical transitions from the valence band to the surface states \((v \rightarrow s)\), we plot \(|M_{v \rightarrow s,\xi}|^2_a\) as a function of \(\theta_k\) in a polar graph in Fig. 3.12(a) for left circularly polarized light \((\varphi = \pi/4)\) and assume \(\Delta > 0\). The red (blue) color denotes the positive (negative) sign of \(|M_{v \rightarrow s,\xi}|^2_a\). We notice that for the upper Dirac cone (UDC) \((\xi = +)\), \(|M_{v \rightarrow s,+}|^2_a > 0\) for positive \(k_y\) and \(|M_{v \rightarrow s,+}|^2_a < 0\) for negative \(k_y\), leading to an asymmetric optical transition dominated by UDC electrons with positive \(k_y\). In contrast, due to the sign reverse of \(|M_{v \rightarrow s,-}|^2_a\) for the lower Dirac cone (LDC), optical transition is dominated by LDC electrons with negative \(k_y\). Since the Fermi velocity also reverses sign between UDC and LDC for a fixed \(k_y\), the optical transition is always dominated by the right-moving branch of surface electrons with a positive \(y\)-direction velocity, as shown schematically by the red-coloring in the surface Dirac cones in Fig. 3.12(a). Similarly, the optical transition from the surface states to conduction bands is dominated by the left-moving branch of surface electrons with a negative velocity, as shown in Fig. 3.12(b).
Figure 3.12. Schematic of preferred optical transitions and polar graphs of asymmetric matrix elements of transitions (a) Schematic picture of optical transitions from the bulk valence band to the Dirac surface states. The asymmetric matrix elements for the transitions are plotted in the polar graph of momentum angle ($\theta_k$) for upper and lower Dirac cones (UDC and LDC), where the sign is denoted by the color (red denotes positive and blue denotes negative). The preferred optical transitions are denoted by the red coloring on the Dirac cone. (b) Schematic picture of optical transitions from the Dirac surface states to the conduction band. The asymmetric matrix element is opposite compared to (a).

3.5 Understanding of the experimental helicity dependent photocurrent with theoretical analysis

3.5.1 Numerical calculation of the photocurrent

We then performed a numerical simulation based on Eq. (3.2) for the photocurrent induced by optical transitions between topological surface states and two bulk bands (one conductance and one valence band with $\Gamma_{6}^{+}$ representation). $\Delta$ is assumed to be positive and the mass of the valence band holes is chosen to be heavier than that of the conduction band electrons. We used the same momentum relaxation time for the excited carriers in bulk states and in surface states for simplicity. (More details of the numerical calculation are described in Methods.) Our numerical calculations reveal the key feature observed in the experimental gate voltage dependence of...
the HDPC, namely, an asymmetric peak whose position is located at the Dirac point. We further separate the photocurrent $J$ into two parts: the current induced by the non-equilibrium distribution of carriers in the surface bands, denoted as $J_s$, and that induced by excited carriers in bulk bands, denoted as $J_b$ (green and blue curves, respectively, in Fig. 3.13). Interestingly, we find that $J_s$ depends monotonically on the chemical potential while $J_b$ has a peak. This suggests that the peak mainly originates from the bulk photocurrent, while the asymmetry originates from the combined contribution of both topological surface states and bulk states. The latter arises because of the difference in mass between valence band holes and conduction band electrons.

Figure 3.13. Numerical calculation of the photocurrent. Calculated photocurrents based on the slab model as a function of the chemical potential. $E_F = 0$ eV denotes the chemical potential located at the Dirac point. The photocurrent contributions from the excited carriers in the surface states (green curve), the bulk bands (blue curve) and the total photocurrent (red curve) are displayed separately.
3.5.2 Schematic picture of helicity dependent photocurrent reaching maximum at the Dirac point

For an intuitive understanding of the peak in the gate voltage dependence of the HDPC, we used a schematic picture of the optical transitions along the $k_y$ direction (Fig. 3.14), where (a), (b), (c) correspond to transitions with different positions of the chemical potential. The circles located in each band refer to the excited carriers that contribute to the net photocurrent. The mass difference between electrons and holes is neglected in the schematic picture for simplicity. Because preferential transitions occur on different branches of the surface states for $v \rightarrow s$ and $s \rightarrow c$, the excited electrons (filled blue circles) and holes (empty red circles) in the surface states induce a photocurrent along the same direction. The comparison between (a), (b) and (c) shows that the photocurrent contribution from the surface states changes little with the chemical potential. However, the bulk states contribute to the photocurrent in a very different manner. When the chemical potential is located at the Dirac point (Fig. 3.14(b)), the photocurrent contribution from the bulk bands (identified by empty blue circles and filled red circles) is maximized along the negative $y$ direction, denoted by the red and blue arrows. As the chemical potential moves away from the Dirac point, either down toward the valence band or up toward the conduction band as shown in Fig. 3.14(a) and (c), respectively, the photocurrent contributed from different bulk bands partially cancels out and decreases (see inset to Fig. 3.14). This physical picture accounts for the HDPC reaching a maximum value at the Dirac point.

3.5.3 Understanding of the asymmetric helicity dependent photocurrent around the Dirac point

The asymmetry of the HDPC around the Dirac point (shown in Fig. 3.7(c)) can be understood from the following three reasons. First, our numerical simulation has revealed the asymmetry of the HDPC (shown in Fig. 3.13), which is induced by the heavier mass of valence band holes, compared to that of conduction band electrons. Second, the transition matrix element between the surface states and the conduction bands is different from that between the surface states and the valence bands. Third, first-principles calculations (Fig. 3.11) show the absence of
Figure 3.14. Schematic picture to explain the peak of HDPC at the Dirac point. (a), (b) and (c) denote the chemical potential below, near and above the Dirac point, respectively. The red dotted arrows denote the preferred transitions from the surface states to conduction bands ($s \rightarrow c$) while the blue dotted arrows denote the preferred transitions from the valence bands to surface states($v \rightarrow s$). The two transitions happen simultaneously and rely on the position of the chemical potential. (a) The chemical potential is below the Dirac point. The excited carriers are denoted by filled circles (electrons) and empty circles (holes). In the valence band, the excited holes are separated into two parts, one denoted by small circles and the other denoted by large circles. As shown in the sub-diagram, the small circles are distributed evenly around the $\Gamma$ point, leading to zero total generated photocurrent. Only the large circles contribute to the net photocurrent. The net photocurrent induced by the bulk carriers is along the negative $y$ direction and denoted by the arrows pointing to the left. The length of the arrows denotes the magnitude of the photocurrent. (b) The chemical potential crosses the Dirac point. The length of the arrows reach a maximum indicating the largest photocurrent. (c) The chemical potential is above the Dirac point. The excited carriers in the conduction band are separated into two parts and the small circles do not contribute a net photocurrent. Therefore, the length of the arrows denoting the net photocurrent decreases.

Conduction band states located at 1.96 eV above the band gap for $(\text{Bi}_{0.5}\text{Sb}_{0.5})_2\text{Te}_3$. Thus, with a photon excitation of 1.96 eV, the HDPC is dominated by optical transitions from the valence band to the surface states ($v \rightarrow s$). As the $v \rightarrow s$ optical transitions become forbidden by populating the surface states with a positive gate voltage, the photocurrent decreases faster. Last, as we use different relaxation times for excited carriers in surface states, valence bands and conduction bands in the numerical calculation (Fig. 3.15), the asymmetry of the calculated HDPC around the Dirac point is tuned by different relaxation times. All three factors...
contributed to the experimentally measured HDPC and can produce the observed asymmetry.

![Figure 3.15](image)

**Figure 3.15.** Numerical calculation of photocurrent using different relaxation times for surface and bulk bands (a) Photocurrent for the case with $\tau_s = 0.5\tau_v$. $\tau_s$, $\tau_c$, and $\tau_v$ denote the relaxation time of the surface states, conduction band and valence band respectively. (b) Photocurrent for the case with $\tau_s = \tau_v$. (c) Photocurrent for the case with $\tau_s = 2\tau_v$.

### 3.5.4 Understanding of the wavelength dependence of the helicity dependent photocurrent

We next comment on the wavelength dependence of the HDPC, based upon the band structure of $(\text{Bi}_{0.5}\text{Sb}_{0.5})_2\text{Te}_3$ in Fig. 3.11. Fig. 3.9 shows that the HDPC reverses sign as the photon energy is varied from 704 nm (photon energy of 1.76 eV) to 1000 nm (photon energy of 1.24 eV). To understand this sign reversal, we note that in Fig. 3.11 the bulk valence bands change from $\Gamma_{-6}$ to $\Gamma_{\pm4/5}$ to $\Gamma_{+6}$ at an energy about 1.5 eV lower than the bulk band gap where the surface states are located. Thus, the HDPC is expected to sensitively depend on photon energies through the optical transitions from different bulk valence bands to surface states. The analysis in Appendix shows that the optical transition between the $\Gamma_{\pm4/5}$ bands and the surface states will not contribute to the photocurrent. It is also suggested that the parameter $\Delta$ in the transition matrix element should have opposite signs for the $\Gamma_{-6}$ and $\Gamma_{+6}$ bands. The sign reversal of $\Delta$ induces the sign reversal of the HDPC at 1.5 eV.
3.5.5 Contributions to helicity dependent photocurrent from other types of spin-split states

Finally, we examine the possibility of contributions to the HDPC from other types of spin-split states, specifically Rashba states induced by band bending [67] and the second excited surface states that were experimentally discovered by ARPES. [76] If we only consider the Rashba effect in the conduction bands (because of the lighter mass), we find that the Rashba effect contributes to an extra photocurrent which is proportional to $-\alpha_R (A_0^2 k_c^2 - sgn(E_F)E_F^2)c_y$, where $\alpha_R$ is the strength of the Rashba effect, $A_0$ is the coefficient of the surface states’ Dirac Hamiltonian, $k_c$ is the cut-off momentum (reference in Appendix). This expression implies that the contribution from the Rashba effect, if it exists, only contributes to the asymmetry of the HDPC peak around the Dirac point. The second excited surface states [59,68] are located around 1.5 eV above the first Dirac point, and thus the optical transition between the two Dirac cones in our photon energy range should exist. This optical transition between the two Dirac cones could contribute to the HDPC according to the analytical study of the photocurrent in appendix. However, we also note from the analytical study that the HDPC from the transitions between the two Dirac cones should increase monotonically as the chemical potential moves up in the gap, which contradicts with our experimental observation of the gate dependent photocurrent.

3.6 Summary and future work

In summary, our systematic measurements provide fundamentally new insights into the HDPC in a 3D TI (Sb doped Bi$_2$Te$_3$). By studying the incidence angle dependence, we unambiguously demonstrate that the CPGE is the physical mechanism underlying the HDPC, and we rule out the photon drag effect. Further, the gate voltage dependence experiment reveals a maximum of the HDPC as the chemical potential approaches the Dirac point. A theoretical model is constructed to qualitatively explain the chemical potential dependence of the HDPC and identify the microscopic origin of the asymmetry of the HDPC when the Fermi energy is tuned above or below the surface Dirac point. The sign change of the HDPC when varying excitation photon energy around 1.5 eV is attributed to different
contributions of photocurrents from the bulk $\Gamma_6^+$ band and $\Gamma_6^-$ band. The demonstration of a robust directional photocurrent that can be systematically controlled by the polarization and wavelength of light and tuned by an electrostatic gate voltage, creates interesting new opportunities for using 3D topological insulators in opto-spintronics. [77–79]

Though we provide a systematic study of the HDPC in 3D TI, the magnitude of this photocurrent controlled by polarization is still small. We have provided ideas on how to improve the magnitude, but a dramatic enhancement is needed for real applications in opto-spintronics. Future work would be associated on improving the sample quality, tuning the wavelength in a broader regime, and maybe taking the same photocurrent measurement in other topological insulators to enhance the helicity dependent photocurrent. On the other hand, the theoretical model that describes the photocurrent in this system could be improved by using a more complex model for the band structure instead of the effective Hamiltonian.
Chapter 4  
Spin-dependent photocurrent in topological insulator- magnetic insulator heterostructures

The emerging field of ‘topological spintronics’ relies on interfacing the helical Dirac surface states of topological insulators (TIs) with magnetism. Heterostructures that combine TIs with insulating magnetic materials are particularly relevant within this context. In this chapter, we extend the photocurrent measurement to heterostructures of yttrium iron garnet (YIG) and 3D topological insulators. Spin-dependent photocurrent (PC) is discovered by the magnetic field sweeping of PC in TI-YIG heterostructures. It is also found that the magnetic field-dependent PC maps out the magnetization state of the YIG layer, by a direct comparison with magneto-optical Kerr effect measurements. We gain insight into the phenomenon by studying the spin-dependent PC as a function of the chemical potential of the TI film, as well as by examining its variation with the temperature and the wavelength of the optical excitation.

4.1 Introduction

The last chapter discussed photocurrent measurements in non-magnetically doped 3D topological insulators induced by coupling between the circularly polarized light and the spin-split surface states. It was shown that the PC measurement was a powerful probe of the spin states of the TIs. For the topological spintronics devices, the photocurrent may be used to probe the spin transport induced by the magnetism. Unlike the PC measurement in the last chapter, an external magnetic
field is introduced here for the photocurrent measurement. The effect of the external field is to create a nonzero magnetization, which provides a spin source for the spintronics devices. With the laser illumination, the equilibrium state is broken and a driving force for spins is created. This driving force could either be the heat gradient from laser heating or nonuniform distribution of the excited carriers by optical transitions. For the TI-magnet heterostructure, the specific magnetic material of this study is an insulating garnet - yttrium iron garnet (YIG). YIG emerges as a good candidate for the topological spintronics devices due to the following advantages. First, the insulating property of YIG prevents any shunting current through the YIG layer, which benefits the magnetization switching using the spin-transfer torque. Second, YIG has a very high Curie temperature that enables spintronics devices at room temperature. Third, due to the ferrimagnetic nature of YIG, the coercive field of YIG is very small, making it relatively easy to switch the magnetization of YIG.

Though the measurement technique of photocurrent is the same as the last chapter, the generation mechanism of the photocurrent is totally different. In the last chapter, the non-zero photocurrent was generated by the angular momentum of the circularly polarized light, which coupled to the spin of the surface states. Here, the balance between the spin up and spin down state is broken by the magnetization of YIG adjacent to the TI. Linearly polarized light can also generate an non-zero photocurrent. The specific mechanisms which can generate the spin dependent photocurrent are listed in the following sections.

4.1.1 Spin Seebeck effect

Spin Seebeck effect is a spin analog of the Seebeck effect, which refers to the generation of a spin current by a thermal gradient. It was first discovered in 2008 by Uchida et.al. [80] that a spin current is injected from a ferromagnet to the attached nonmagnetic metal under the influence of a thermal gradient. This effect was later demonstrated to be a universal aspect of ferromagnets. [81–84] For a spin Seebeck device which consists of a ferromagnet and an nonmagnetic material, the injected spin current into the nonmagnet is then converted into a transverse charge current due to the inverse spin Hall effect. [54] Therefore, the thermal gradient is eventually transformed into a charge current as in conventional Seebeck
devices. However, unlike the conventional Seebeck effect, the heat current and the charge current are separated in the spin Seebeck device. Therefore, the challenge of simultaneous optimization of thermal conductivity and electrical conductivity is circumvented. The discovery of spin Seebeck effect opened up a new field, called spin caloritronics [85], which studies the relationships between heat and spin transport. Several technological applications have been proposed for spin caloritronics, [86–89] especially in the field of waste heat recovery.

Johnson and Silsbee [90] have developed a model for the direct electrical injection of a spin current across the interface of a ferromagnet and a normal metal. It is based on the simple Stoner model that an imbalance between the populations of spin-up and spin-down electrons in the conduction band of a ferromagnetic metal induces a spin-polarized charge current. However, the spin Seebeck effect can not be simply explained by this model owing to the facts that 1) it even occurs in an insulating ferromagnet without free carriers and 2) the spin injection length scale far exceeds the spin flip diffusion length of conduction electrons. In order to understand the physics of the spin Seebeck effect, the spin current carried by spin waves (magnons) have to be taken into account. Detailed theory arguments can be found in ref. [91]. This section focuses on experiments of the spin Seebeck effect.

The spin Seebeck effect have been observed in both transverse and longitudinal orientations. The transverse spin Seebeck effect (TSSE) refers to a spin injection into the non-magnet transverse to the thermal gradient in the magnetic layer, illustrated in Fig. 4.1(a). As a contrast, the longitudinal spin Seebeck effect (LSSE) is based on a thermal gradient across the heterostructure, thus parallel to the spin injection direction. (Fig. 4.1(b)) People also distinguish them as non-local thermal spin injection and local thermal spin injection. With the light illumination, the induced thermal gradient is vertical and therefore, only the LSSE is relevant to the charge current generated by light in TI.

### 4.1.2 Photo-spin-voltaic effect

The photo-spin-voltaic effect (PSV) refers to the generation of a spin voltage induced by optical transitions in a non-magnet adjacent to a magnetic insulator. This was first reported by Prof. Mingzhong Wu’ group at Colorado State University in a heterostructure of platinum and YIG. The conventional photo-voltaic effect
Figure 4.1. Schematic illustrations of the spin Seebeck effect (a) Longitudinal spin Seebeck effect (b) Transverse spin Seebeck effect. Figure reproduced from ref [13].

is induced by a built-in electric field that drives excited carriers and results in an electric voltage, whereas the PSV is originated from the unbalanced diffusion of spin-up and spin-down carriers at the interface of non-magnet and magnetic insulator. Therefore, the discovery of the PSV provides an additional method for spin injection besides the spin Seebeck effect and the spin pumping with the help of microwaves. [92]

Fig. 4.2(a) illustrates the mechanism of the spin injection induced by PSV in the heterostructure of platinum and a magnetic insulator (MI). At the interface, a few atomic layers of Pt is magnetized by YIG due to the proximity-induced magnetism [45, 46, 93, 94], thus creating an imbalance in the chemical potential of the spin up and spin down electrons ($\mu_\uparrow - \mu_\downarrow > 0$). As a consequence, for optical excitations in this magnetized layer, spin-down electrons are more likely to be excited than spin-up electrons. The excited spin-down electrons and spin-up holes diffuse into the Pt away from the interface. The difference in the diffusion length between holes and electrons induces a net spin current, as shown in Fig. 4.2(b). The spin injection into Pt is then converted to a lateral charge current, akin to the LSSE, by the inverse spin Hall effect. The PSV can also happen in the heterostructure of TI-YIG since the TI also has a strong spin-orbit coupling as Pt.
Figure 4.2. Schematic illustrations of the photo-spin-voltaic effect (a) Schematic of the spin injection induced by light illumination (b) Detailed spin injection process due to the electron and hole diffusion imbalance. Figure reproduced from ref [14].

4.1.3 Dirac cone shift in the momentum space

The topological surface states of a TI can be described by a massless Dirac equation,

\[ H_0 = v(\sigma_x k_y - \sigma_y k_x) \]  

where \( v \) is the Dirac velocity. If a ferromagnetic film with magnetization \( \mathbf{m} \) is attached to the surface of the 3D TI, the Hamiltonian of the surface states are expressed as,

\[
H = H_0 + H_m = \sigma_x(vk_y - m_x) - \sigma_y(vk_x + m_y) - m_z\sigma_z
\]

\[
E(k) = \pm \sqrt{(vk_y - m_x)^2 + (vk_x + m_y)^2 + m_z^2},
\]

where \( H_m \) is the Zeeman energy. [15] For an in-plane magnetization \( (m_z = 0) \), the linear dispersion at the Dirac point is still protected by the mirror symmetry. From Eq. 4.2, we can see that the Dirac point \( (E=0) \) is shifted away from the \( \Gamma \) point. The energy dispersion of the surface states can explain this shift more intuitively, as shown in Fig. 4.3. The left panel shows the Dirac dispersion of the surface states in the mirror plane without any magnetization. The right one shows the change of the dispersion with \( \mathbf{M} \) perpendicular to the mirror plane. Due to the Zeeman
energy, the parallel spin branch shifts up while the antiparallel spin branch shift down. As a consequence, the crossing of the two spin branches shifts away from the $\Gamma$ point in the momentum space.

![Figure 4.3. Schematics of the Dirac cone shift by the in-plane magnetization](image)

(a) The surface states dispersion without the Zeeman field. (b) The surface states dispersion with the Zeeman field induced by the in-plane magnetization. Figure reproduced from ref [15].

With a shifted Dirac cone, the carrier excitation from the surface states to the bulk states can generate bulk carriers with a net momentum, as shown in Fig. 4.4. The net momentum reverses direction as the magnetization reverses direction. Therefore, the light excitation generates a net photocurrent. The direction of the photocurrent is perpendicular to the magnetization direction since the shift of the Dirac cone in the momentum space is perpendicular to the magnetization direction. Therefore, the Dirac cone shift in an in-plane magnetic field is another possible source of the field dependent photocurrent in the TI-YIG heterostructure.

### 4.2 Photocurrent measurements in TI-YIG heterostructures

#### 4.2.1 Field dependent photocurrent

The TI-YIG heterstuctures were fabricated by the collaboration of our group with Prof. Mingzhong Wu’s group at Colorado State. The YIG thin films were deposited by sputtering on GGG substrates by our collaborators. We grew 10 QL
Figure 4.4. **Schematic of the optical transition between the shifted Dirac cone and the bulk conduction band.** The excited electrons in the bulk band are not symmetric around $\Gamma$ point, thus inducing a net momentum.

$(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ thin films by molecular beam epitaxy on top of 20 nm thick YIG. Atomic force microscopy was used to examine the roughness of the $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ surface. It was found that growing a seed layer (1-2 nm) of Bi$_2$Se$_3$ on top of YIG could improve the surface roughness of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ that was grown after.

We reported photocurrent measurements with an in-plane magnetic field ($B_{\text{in}}$) applying perpendicular to the device channel as shown in FIG. 4.5(a). The p-polarized He-Ne laser was shed in the x-z plane with an incidence angle of 33°. The oblique incidence was not necessary to generate the field dependent photocurrent, but more convenient for the imaging of the beam spot with a camera. The method of the photocurrent measurement was the same as that discussed in the last chapter. We discovered field dependent photocurrents at both room temperature (293K) and 25K. The photocurrents of device A were shown in Fig. 4.5(b), where offset photocurrents had been deducted. Device A was made on a film that consisted of 10 nm $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$, 1-2 nm Bi$_2$Se$_3$ seed layer and 20 nm YIG. We noted that the photocurrent variation with the field was a hysteresis at each temperature. Besides a linear variation with the field, the photocurrent changed dramatically at the coercivity (9 Gauss at 293K and 30 Gauss at 25K) and saturated at large
fields. The total change was around 2 pA. We also noticed that the direction of the photocurrent’s change at 293K at the coercivity was opposite to the change at 25K. Since YIG is a ferrimagnetic insulator with an in-plane easy axis and a small coercivity, the natural question to ask is whether the hysteretic variations of the photocurrents could match with YIG’s magnetization. In order to address this question, the magneto-optical Kerr effect was used to study the in-plane magnetism of the YIG thin film on the same device.

4.2.2 Longitudinal magneto-optical Kerr effect of YIG

The Kerr rotation of YIG is reported in this section. It was clearly shown that the YIG’s magnetization showed a hysteretic variation with the in-plane field sweeping. Under the same sweeping rate of the magnetic field, the coercivity of the hysteresis matched with that of the photocurrents in the TI layer at both temperatures, as shown in Fig. 4.6. (The exact value of the coercivity was dependent on the sweeping rate, thus the comparison must be under the same sweeping rate.) Thus, it was demonstrated that the field dependent photocurrent originated from the YIG’s magnetization. As stated in the introduction section, the exact generation mechanism should be among the three, the spin Seebeck effect, the photo-spin-voltaic effect, and the Dirac cone shift. However, further measurements were needed to elucidate the exact origin of the field dependent photocurrent.
Figure 4.6. Longitudinal MOKE of the YIG layer in device A (a) The longitudinal Kerr rotation of the YIG thin film at room temperature (293 K). (b) The longitudinal Kerr rotation of the YIG thin film at 25 K.

4.2.3 The influence of the Bi$_2$Se$_3$ seed layer

We found growing a seed layer of Bi$_2$Se$_3$ on top of YIG could help improve the surface quality of the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ film that was grown on top. However, for the heterostructure of TI-YIG, the interface quality was also important. The photocurrent generation may rely on the proximity effect at the interface. Therefore, we conducted the photocurrent measurement in another device (device B) of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ -YIG heterostructure without the Bi$_2$Se$_3$ seed layer. The sample thickness and Sb doping level of device B were similar as device A. As shown in Fig. 4.7, the field dependent photocurrents of device B were larger than that of device A at both room temperature and 25K. It was thus demonstrated that directly interfacing (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ with the YIG substrate yielded a larger field dependent photocurrent, though the top surface was not as smooth. In the gate voltage dependence study discussed in the next section, a further comparison between device A and device B will be made.
4.3 The variation of the field dependent photocurrent with the top gate

To explore the relation between the field dependent photocurrent in the TI-YIG heterostructure and the surface states of TI, a top gate was utilized in each device to tune the chemical potential. The device fabrication process was already introduced in the Methods chapter. The top gate consisted of 30 nm Al₂O₃ and 300 nm ITO. The field dependent photocurrents were measured with tunable gate voltages in both device A (with the Bi₂Se₃ seed layer) and device B (without the Bi₂Se₃ seed layer). Transport measurements of the Hall resistance and the longitudinal resistance were taken to identify the position of the chemical potential. For both devices, the Dirac point, identified by the zero Hall resistance or the peak of the longitudinal resistance, was shown to be near zero voltage (Fig. 4.8(a) and Fig. 4.7(a)). Fig. 4.8(b) shows the photocurrent in device A at 25K with sweeping magnetic field (Bₘₙ) at multiple gate voltages, ranging from +10V to -8V. The photocurrent variation consisted of two field dependent features, a linear dependence on the field and a hysteresis with abrupt changes at the coercivity. Both varied with the top gate voltage. We plotted the slope of the linear dependence (Iₚh_slope, red curve) and the saturated value of the change around the coercivity (Iₚh_Sat, blue curve) as
a function of the gate voltage in Fig. 4.8(c). Around the Dirac point, the slope was largest while the saturation value of the hysteresis ($I_{ph\_Sat}$) passed zero. The sign reversal of $I_{ph\_Sat}$ denoted that the change of photocurrent at the coercivity reversed direction. Moreover, the absolute value of $I_{ph\_Sat}$ was largest when the surface states were most populated (at +10V) and reached a saturated value when the surface states are depleted (large negative gate voltages).

Figure 4.8. Field dependent photocurrent varies with the top gate. (a) The Hall resistance (red curve) and the extracted 2D carrier concentration ($n_{2D}$) as a function of the top gate voltage. (b) Field dependent photocurrents at 25 K at variable gate voltages ranging from 10 V to -8 V. (c) The saturated photocurrent at a large positive field (blue) and the slope of the linear dependence of photocurrent at large fields (red) as a function of the gate voltage.

Similar photocurrent experiments were taken in device B at 25K, as shown in Fig. 4.9. The peak of $R_{xx}$ in Fig. 4.9(a) denoted the Dirac point. The gate voltage dependence of the photocurrent was similar as that of device A. The variation of the hysteresis saturation value and the slope of the linear dependence with the gate voltage (Fig. 4.9(c)) were not affected by the seed layer. However, we noticed that
the absolute value of the field dependent photocurrent was much larger in device B than that of device A. Therefore, we demonstrated that the proximity effect or the spin injection at the interface that induced the photocurrent was impeded by the seed layer. The rest studies of the field dependent photocurrent were carried out in the TI-YIG heterostructure without the seed layer.

Figure 4.9. Field dependent photocurrent in device B with variable gate voltages. (a) The longitudinal resistance ($R_{xx}$) as a function of the top gate voltage. (b) Field dependent photocurrents at 25 K under variable gate voltages ranging from 10 V to -12 V. (c) The saturated photocurrent at a large positive field (blue) and the slope of the linear dependence of photocurrent at large fields (red) as a function of the gate voltage.
4.4 Unusual features in the hysteresis of the field dependent photocurrent

4.4.1 Temperature dependence of the photocurrent

It was clearly shown by Fig. 4.9 that the hysteresis of the field dependent photocurrent had additional features besides the main jump at the coercivity. However, it was not observed at room temperature (Fig. 4.7(a)). We studied the temperature dependence from 25 K to 130 K in device B, as shown in Fig. 4.10. The unusual features present at 25 K started to disappear as the temperature rose, and totally went away at 130 K. From the study of YIG’s magnetization at 25 K by MOKE, we could learn that these side features did not originate from YIG. Instead, 130 K can correspond to the Curie temperature of the proximity induced magnetism in TI, reported by ref [46]. Further studies were taken by exploring the light polarization dependence of the unusual features.

4.4.2 Polarization dependence of the photocurrent

The field dependent photocurrents under a gate voltage of 8 V were measured at 25 K with p-polarized, circularly polarized and s-polarized excitations, as shown in Fig. 4.11. The saturated value of the hysteresis in the field dependent photocurrent was similar for each polarization. However, the unusual features of the hysteresis were only present in the p-polarized light induced photocurrent. The field dependent photocurrent under s-polarized or circularly polarized light was a square loop. Besides the shape of the hysteresis, the coercivity of the p-polarized light induced photocurrent (~ 40 Gauss) was significantly smaller than that of the photocurrent under the s-polarized or circularly polarized light (~ 60 Gauss). In the top right panel of Fig. 4.11, the magnetization of YIG was studied on the same piece of sample by the longitudinal MOKE. The Kerr rotation of YIG did not have any complex features in the variation with the in-plane field and the coercivity was similar to that of the photocurrent under s-polarized or circularly polarized light. Therefore, we demonstrated that the unusual features of the photocurrent variation must be induced by the p-polarized light.

In the temperature dependence study, it was clearly shown that the unusual
Figure 4.10. The variation of the field dependent photocurrent with temperature. The photocurrent with p-polarized light at various temperatures. The unusual features of the hysteresis disappeared at 130K.

features under p-polarized light disappeared near 130 K. Thus, we compared the field dependent photocurrents between s and p polarized light at 130 K, as shown in Fig. 4.12. They looked similar except for a small difference in the coercivity. The difference in the coercivities decreased from 20 Gauss (at 25K) to 5 Gauss (at 130K). From this perspective, it was confirmed that the p-polarized light induced the unusual features in the photocurrent hysteresis, which had a Curie temperature near 130 K. There were no further measurements that could elucidate the exact origin of the polarization induced complexity in the field dependent photocurrent, but we highly suspected the photo-induced magnetic anisotropy [95–97] was the origin. However, to focus on the major story, we would only discuss the field dependent photocurrents under s-polarized excitations.
Figure 4.11. Field dependent photocurrents at different polarizations. (25K)
The photocurrents induced by p-polarized, circularly polarized and s-polarized light. The top right panel shows the Kerr rotation of YIG on the same piece of sample.

Figure 4.12. Field dependent photocurrent under different polarizations at 130K. The photocurrents induced by p-polarized and s-polarized light at 130K.

4.4.3 Chemical potential dependence of the photocurrent under s-polarized light

Last, we need to study whether the chemical potential dependence of the photocurrent was subject to the polarization of light. Fig. 4.13 shows the variation of the field dependent photocurrent with the gate voltage at 25 K under the s-polarized light. The direction of the hysteresis still changed between 0V and -1.5V. The variation of the photocurrent with the gate voltage for s-polarized light was the
same as that of p-polarized light, regarding the saturation value of the hysteresis and the slope of the photocurrent at large fields. Therefore, the variation of the photocurrent with the chemical potential and the variation with the light polarization were independent behaviors. Due to the independence, we could comprehend the chemical potential dependence of the photocurrent without a good understanding of the polarization dependent photocurrent.

![Figure 4.13. Gate voltage dependence of the photocurrent under s-polarized light.](image)

Figure 4.13. Gate voltage dependence of the photocurrent under s-polarized light. The field dependent photocurrent induced by s-polarized light varies with the gate voltage. The direction of the hysteresic change reverses direction as that of the p-polarized light induced photocurrent.

### 4.5 Wavelength dependence of the field dependent photocurrent

We gained more insights into the field dependent photocurrent by exploring the effect of using light sources with different wavelengths. The change of wavelength was realized by using a supercontinuum laser from Prof. Roland Kawakami’s group at Ohio State. The laser generated a broad spectrum of light, ranging
from 400 nm to 2000 nm. A monochromator was used to filter out a narrow bandwidth (2 nm) of light at the desired wavelength. Because of the optical limit of the optics, the far infrared light was ruled out in this study. The light near 400 nm was also ruled out due to the damage to the TI thin film from the high-energy photons. Four representative wavelengths were chosen in the viable wavelength range. The intensity of the laser was kept constant at 1 mW. Fig. 4.14 shows the gate voltage dependence of the saturated photocurrent under the four wavelengths. The saturated photocurrent was extracted from the magnetic field sweeping of the photocurrent. For all four wavelengths, the saturated photocurrents showed monotonic variations with the gate voltage, similar to the photocurrent under 633 nm, as shown in Fig. 4.9(c). However, we noted that for 950 nm, the saturated photocurrent at -10V was opposite to the saturated photocurrent at other wavelengths under the same gate voltage. Moreover, the zero crossing, at which voltage the saturated photocurrent changed sign, varied with the wavelength. It changed from -2V for 480nm to -4V for 580nm, further to -7V for 700nm. Besides, the amplitude of the saturated photocurrent decreased with the decreasing wavelength. These are the major results of the wavelength dependence study.

4.6 Underlying mechanism of the field dependent photocurrent

4.6.1 Discussion of the experimental results

The photocurrent experiments reported in previous sections have discovered the following facts in (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$-YIG heterostructures.

1. The photocurrent variation with the in-plane magnetic field showed a hysteretic change with a coercivity similar to the coercivity of YIG’s magnetization. Under s-polarized light, the hysteresis could be decomposed into a square loop and a linear dependence on the field.

2. For heterostructures with the Bi$_2$Se$_3$ seed layer at the interface, the saturated value of the hysteresis was much smaller than that in heterostructures without the Bi$_2$Se$_3$ seed layer.
Figure 4.14. The gate voltage dependence of the saturated photocurrent under different wavelengths. The saturated photocurrent under 480 nm, 580 nm, 700 nm and 950 nm light illumination as a function of the gate voltage.

3. The field dependent photocurrent varied with the gate voltage (chemical potential). Populating the topological surface states increased the saturated photocurrent. As the chemical potential approached the valence band edge, the saturated photocurrent decreased and finally reversed direction. Besides, the slope of the linear dependence on the field in the photocurrent was largest at the Dirac point.

4. The variation of the saturated photocurrent with the gate voltage depended on the wavelength of the excitation. For relatively short wavelengths (480 nm - 700 nm), the saturated photocurrent was relatively smaller and reversed direction at certain gate voltages. For a longer wavelength (950 nm), the saturated photocurrent was significantly larger and never reversed direction as the gate voltage was swept from 8V to -12V.

These findings can be used to analyze the underlying mechanism of the field dependent photocurrent. In the introduction section, we had proposed three possible mechanisms, the longitudinal spin-Seebeck effect (LSSE), the photo-spin-
voltaic effect (PSV) and the Dirac-cone shift with the in-plane field. For each mechanism, it could generate a photocurrent that depended on the in-plane field. We would discuss the consistency of the experimental results with each mechanism in the next few sections.

4.6.2 Longitudinal spin Seebeck effect

Here, the LSSE describes the spin injection from YIG to the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ thin film driven by the vertical heat gradient induced by the laser heating. The vertical spin injection is converted to an in-plane charge current flowing in the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ by the inverse spin Hall effect. Once the spin direction inverses as the magnetization of YIG flips, the charge current will reverse the direction. Therefore, the photocurrent generated by the LSSE agrees with the first finding in our experiments. Further, the magnitude of this photocurrent depends on the spin injection efficiency, which would be influenced by the Bi$_2$Se$_3$ seed layer at the interface. Thus, the second finding does not contradict with the LSSE as well. The gate voltage dependence of the photocurrent (the third finding) is critical for analyzing the underlying mechanism. For the LSSE, the direction of the photocurrent is determined by the direction of the heat gradient and the polarity of the spin-orbit coupling strength ($\lambda_{so}$). Both should not change with the chemical potential, thus the sign reversal of the saturated photocurrent in the gate voltage scan cannot by explained by the LSSE. An experimental demonstration has been reported in ref [16], where the LSSE was studied in the TI-YIG heterostructure. The voltage created by the LSSE did not reverse direction when tuning the chemical potential, as shown in Fig. 4.15 (copied from ref [16]). Therefore, the LSSE does not satisfy the gate voltage dependence of the photocurrent from our measurements. As for the wavelength dependence, the LSSE induced by the laser heating should be more prominent under shorter wavelength (480nm) as compared to the longer wavelength (950nm). In the photon energy range of our measurement, the shorter wavelength, the shorter penetration depth, thus a larger heat gradient. However, we observed a smaller photocurrent under 480nm, contradicting with the LSSE. In sum, the LSSE is not the major cause of the field dependent photocurrent.
Figure 4.15. The LSSE study in TI-YIG heterostructures from ref [16]. (a) Temperature dependence of longitudinal resistance $R_{xx}$ for $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$-YIG heterostructures with $x$ ranging from 0 to 1. (b) The LSSE signal in $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$-YIG heterostructures (with different Sb ratios) as a function of the in-plane field. The direction of the hysteresis did not change with the chemical potential tuning.

4.6.3 The Dirac cone shift with the in-plane field

As explained in the introduction section, the Dirac cone under an in-plane magnetic field will not open a gap at the Dirac point. Instead, the Dirac cone will be shifted away from the $\Gamma$ point in the momentum space. Therefore, the optical transitions from the Dirac surface states to the bulk bands could generate a net momentum due to the shift of the Dirac cone in the momentum space. Now let’s discuss whether this mechanism can explain the experimental results of the field dependent photocurrent.

Since the Dirac cone shift depends on the in-plane magnetic field or magnetism, the generated photocurrent varies with the in-plane field. The proximity induced magnetism in the TI has been reported in TI-MI heterostructures [45, 46, 98, 99], thus a hysteresis would be present in the field dependent photocurrent. This is consistent with the experimental results. When a few atomic layers of $\text{Bi}_2\text{Se}_3$ were
introduced into the interface of the TI-YIG heterostructure, the proximity induced magnetism in \((\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3\) would be hindered by the seed layer, thus decreasing the photocurrent. As for the sign reversal of the saturated photocurrent in the gate voltage scan, what determines the direction of the photocurrent is important. For the mechanism of the Dirac cone shift, the photocurrent direction is determined by the shift direction in the momentum space, which depends on the magnetization direction. The chemical potential tuning cannot change the shift direction, thus the sign reversal of the saturated photocurrent is not expected under the Dirac cone shift mechanism. However, the linear dependence on the field, though very small, could be the consequence of the Dirac cone shift. The slope direction of the linear dependence is consistent with the Dirac cone shift induced photocurrent. Moreover, the fact that the slope maximized around the Dirac point provides another evidence that the linear dependence is correlated with the Dirac surface states. To summarize, the Dirac cone shift is not responsible for the hysteresis in the field dependent photocurrent, but might be the cause of the linear dependence on the field.

### 4.6.4 Photo-spin-voltaic effect

The PSV in TI-YIG heterostructure is based on the proximity induced magnetism in the TI layer. The spin injection into the TI bulk is induced by optical transitions in the magnetized TI. A current is then generated by the inverse spin Hall effect. The direction of the current is dependent on the magnetization of the TI layer. The proximity induced magnetism in TI-MI heterostructures has been theoretically studied. [50] The spin paramagnetism dominated the Dirac surface states while the orbital diamagnetism dominated the bulk states of TI. The distinctive behaviors between the surface states and the bulk states induce the dependence of the overall magnetism on the chemical potential.

The experimental results of the photocurrents are consistent with the PSV. First, the hysteresis in the field dependent photocurrent is due to the proximity induced magnetism in the TI layer adjacent to the YIG. Secondly, the \(\text{Bi}_2\text{Se}_3\) seed layer at the interface may hinder the proximity effect, thus decreasing the photocurrent. Thirdly, with the gate voltage tuning, the sign reversal of the saturated photocurrent is induced by the the direction change of the overall magnetization. As the
chemical potential approached the valence band edge (a negative gate voltage), the magnetization was dominated by the bulk band diamagnetism (opposite to YIG’s magnetism). As the chemical potential was tuned up (a positive gate voltage), the spin paramagnetism from the surface states dominated the overall magnetization. Thus, the photocurrent originating from the proximity induced magnetization reversed direction in the gate voltage scan. Last, the wavelength dependence of the photocurrent does not contradict with the mechanism as well. In the wavelength range of the excitation, the longer wavelength, the longer penetration depth. Thus, for 950 nm, the light intensity penetrating to the TI-YIG interface was stronger than that of 480 nm. This is why the saturated photocurrent at 950 nm is significantly larger than the photocurrent under shorter wavelengths. Another important fact is that the saturated photocurrent reverses direction at different gate voltages for different wavelengths. As shown in Fig. 4.16, the excitation at 480 nm not only excite carriers in the surface states but also excite carriers far below the chemical potential in the bulk valence band. However, the excitation at 950 nm can only excite carriers in the surface states. Therefore, the field dependent photocurrent for 480 nm reverses direction at a small gate voltage where the chemical potential is still far away from the valence band edge. For 950 nm, the photon energy is small and cannot excite carriers from the bulk band, thus the field dependent photocurrent keeps the same direction in the voltage scan. In sum, the photo-spin-voltaic effect is the major cause of the field dependent photocurrent since the experimental results can be explained by this mechanism.

4.6.5 Anomalous Hall effect

The fourth mechanism of generating a field dependent photocurrent was not discussed in the introduction chapter, but is not negligible. The anomalous Hall effect can create a voltage perpendicular to the charge current and the magnetization direction. For TI-YIG heterostructures, the induced magnetism in a few atomic layers of TI adjacent to the YIG is the source of the magnetization in the anomalous Hall effect. The charge current was originated in the excited carriers at the TI-YIG interface which is driven by the electrostatic field created by the top gate. The direction of the electrostatic field was vertical and the magnetization was along the field direction. Therefore, the voltage induced by the anomalous Hall effect
Figure 4.16. Schematic of optical excitations in topological insulators under different wavelengths. The excitation under 480nm light are denoted by the blue arrow while the excitation under 950nm light is denoted by the red arrow.

was along the photocurrent measurement direction, as shown in Fig. 4.5. Further, since the charge current was driven by the gate voltage, the charge current would reverse direction when the gate voltage changed from positive to negative. Thus, the photocurrent would reverse direction near zero gate voltage, as we measured. Therefore, the anomalous Hall effect can satisfy the gate voltage dependence of the photocurrent. However, the wavelength dependence of the photocurrent contradicts with the anomalous Hall effect. The direction of the photocurrent can not be altered by changing the wavelength since the direction was only determined by the electrostatic field from the gate. Therefore, the anomalous Hall effect is not the major cause of the field dependent photocurrent in our measurements.

We have discussed the consistency of the experimental results with different mechanisms, as shown in Table 4.1. In summary, only the photo-spin-voltaic effect (PSV) can explain all the experimental discoveries of the field dependent photocurrent. Therefore, we believe that the field dependent photocurrent is induced by the PSV. However, The Dirac cone shift and the anomalous Hall effect can explain some of the results. These two effects may have a small contribution to the field dependent photocurrent.
Table 4.1. Consistency of the experimental results with different mechanisms

<table>
<thead>
<tr>
<th></th>
<th>LSSE</th>
<th>Dirac cone shift</th>
<th>PSV</th>
<th>AHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{ph_Sat}$ versus $V_{TG}$</td>
<td>×</td>
<td>×</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>$I_{ph_slope}$ versus $V_{TG}$</td>
<td>×</td>
<td>○</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>Wavelength dependence</td>
<td>×</td>
<td>×</td>
<td>○</td>
<td>×</td>
</tr>
</tbody>
</table>

4.7 Summary and future work

A comprehensive study of the field dependent photocurrent in TI-YIG heterostructures has been reported in this chapter. The photocurrent in TI varied with the in-plane magnetic field hysteretically at both room temperature and cryogenic temperatures. By comparing the photocurrent to the Kerr rotation of YIG, we showed that the coercivity of the photocurrent was the same as the coercivity of YIG’s magnetization. By exploring the gate voltage dependence and the wavelength dependence of the photocurrent, we demonstrated that the cause of the photocurrent was the photo-spin-voltaic effect (PSV), which was induced by the spin diffusion into the bulk of TI. Therefore, the field dependent photocurrent can be called as 'spin-dependent photocurrent'. It can be used as a sensor of the magnetization in the TI-YIG heterostructure, which is of practical significance for spintronics devices. Especially for a magnetic insulator like YIG, it is not easy to probe the magnetization, but the field dependent photocurrent opens up a new path. Fig. 4.17 shows a demonstration of using the photocurrent as a magnetization sensor. When pulsing the magnetic field to orient the magnetization, a non-zero photocurrent was observed. Once the direction of the magnetization was reversed by pulsing a negative field, the photocurrent reversed direction. As a consequence, the photocurrent in TI can be used as a powerful probe of the magnetization in the heterostructure.

Another discovery of the spin dependent photocurrent is the sensitivity to the polarization of the excitation. For p-polarized light, a more complex field dependent photocurrent was generated, which was not a square loop. The unusual features in the hysteresis were signatures of polarization induced magnetic anisotropy in the heterostructure. However, our study did not unveil the underlying mechanism of the polarization induced magnetism. Further work is needed for a comprehensive understanding of the polarization dependence. Besides, though it was demonstrated that the field dependent photocurrent was greatly enhanced by applying a gate
Figure 4.17. Demonstration of sensing the magnetization by the photocurrent measurement. When pulsing the magnetic field, the magnetization of YIG is oriented. Correspondingly, a non-zero photocurrent is observed. The direction of the photocurrent depends on the direction of the magnetic field.

voltage at 25K, the photocurrent at room temperature was not tuned in our study since the gate broke down easily at room temperature. In order to utilize this effect for real-world applications, future work in enhancing the photocurrent at room temperature is necessary. According to the insights gained in our studies, tuning the Bi/Sb ratio and using a near-infrared red light could be helpful.
Appendix

Theoretical analysis and numerical calculation of photocurrent

This Appendix is based on the supplementary materials in the paper titled as "Helicity dependent photocurrent in electrically gated topological insulators" submitted to Nature Communications.

1 Theoretical analysis of photocurrent

1.1 Equation of photocurrent

We start the derivation of photocurrent equation based on the assumption that the momentum of light is small and can be ignored. Thus, only vertical optical transitions is considered. The photocurrent with a fixed photon energy \( \hbar \omega \) is expressed as

\[
J = -e \sum_{\eta} \sum_{\mathbf{k}} v_{\mathbf{k},\eta} (f_{\mathbf{k},\eta} - f_{\mathbf{k},\eta}^0)
\]

, where \( \mathbf{k} = (k_x, k_y) \), \( e \) is the electron charge, \( \eta \) represents band index, \( v \) is the velocity of electrons for band \( \eta \) and \( f_{\mathbf{k},\eta}(f_{\mathbf{k},\eta}^0) \) is the equilibrium Fermi distribution function for band \( \eta \) with momentum \( \mathbf{k} \) with(without) light excitation. We obtain the distribution function through the Boltzmann equation \( \frac{df_{\mathbf{k},\eta}}{dt} = \sum_{\eta'} T_{\phi_{\mathbf{k},\eta'} \rightarrow \phi_{\mathbf{k},\eta}} (f_{\mathbf{k},\eta'}^0 - f_{\mathbf{k},\eta}^0) + I_{\text{relax}}[f_{\mathbf{k},\eta}] \), where \( T_{\phi_{\mathbf{k},\eta'} \rightarrow \phi_{\mathbf{k},\eta}} = \frac{2\pi}{\hbar} |\langle \phi_{\mathbf{k},\eta'} | H_{\text{int}} | \phi_{\mathbf{k},\eta} \rangle|^2 \delta(E_{\mathbf{k},\eta} - E_{\mathbf{k},\eta'} - \hbar \omega) \) is the transition rate derived from Fermi’s golden rule and \( I_{\text{relax}}[f_{\mathbf{k},\eta}] \) describes the relaxation of excited carriers from states \( \phi_{\mathbf{k},\eta} \). Under the assumption that the
momentum relaxation time is much faster than the energy relaxation, we have $I_{\text{relax}}[f_{k,\eta}] = -\frac{f_{k,\eta} - f_{k,\eta}^0}{\tau_\eta}$, where $\tau_\eta$ is the momentum relaxation time of band $\eta$.

When the system reaches its equilibrium state, $\frac{df_{k,\eta}}{dt} = 0$, we find that $f_{k,\eta} = f_{k,\eta}^0 = \sum_{\eta'} \tau_\eta T_{\phi_{k,\eta'} \rightarrow \phi_{k,\eta'}}$. Thus, the photocurrent can be written as

$$J = -\frac{2\pi e}{\hbar} \sum_{k,\{\eta,\eta'\}} (\tau_\eta \mathbf{v}_{k,\eta} - \tau_{\eta'} \mathbf{v}_{k,\eta'}) |\phi_{k,\eta'}| |H_{\text{int}}| |\phi_{k,\eta}| \left| \left( f_{k,\eta'}^0 - f_{k,\eta}^0 \right) \delta(E_{k,\eta} - E_{k,\eta'} - \hbar \omega) \right|$$

, where the summation $\langle \eta', \eta \rangle$ indicates pairs of the initial and final states. The interaction Hamiltonian $H_{\text{int}}$ is derived as $-\frac{\epsilon}{\hbar} \frac{\partial H_0}{\partial k} \cdot \mathbf{A}$ based on the minimal coupling $k \rightarrow \Pi = k - \frac{\epsilon}{\hbar} \mathbf{A}$ with $\mathbf{A}$ as the vector potential. Based on the $k \cdot p$ theory, one can obtain the Hamiltonian as $H_{k,p} = (\epsilon_n + \frac{\hbar^2}{2m} k^2) \delta_{nn'} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{P}_{nn'}$, on the basis $|n\rangle$ with $n = 1, 2, 3...$ and $\mathbf{P}_{nn'} = \langle \eta | \hat{p} | n \rangle$ describes the coupling between states $|n\rangle$ and $|n'\rangle$ with $\hat{p}$ as the momentum operator. Further, by using the second order perturbation to project irrelevant states $|l\rangle$ to the states we are considering, we can obtain an effective Hamiltonian $(H_{0, \text{eff}})_{nn'} = (\epsilon_n + \frac{\hbar^2}{2m} k^2) \delta_{nn'} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{P}_{nn'} + \frac{\hbar^2}{2m^2} \sum_{l \neq n, n'} (\mathbf{k} \cdot \mathbf{P}_{nl})(\mathbf{k} \cdot \mathbf{P}_{l'n'}) \left( \frac{1}{\epsilon_n - \epsilon_l} + \frac{1}{\epsilon_n - \epsilon_l} \right)$. Thus, the interaction Hamiltonian reads $(H_{\text{int}})_{nn'} = -\frac{\epsilon}{m} \mathbf{A} \cdot \mathbf{P}_{nn'} - \frac{e \hbar}{m} (\mathbf{A} \cdot \mathbf{k}) \delta_{nn'} - \frac{e \hbar}{2m^2} \sum_{l \neq n, n'} ((\mathbf{A} \cdot \mathbf{P}_{nl})(\mathbf{k} \cdot \mathbf{P}_{l'n'}) + (\mathbf{k} \cdot \mathbf{P}_{nl})(\mathbf{A} \cdot \mathbf{P}_{l'n'})) \left( \frac{1}{\epsilon_n - \epsilon_l} + \frac{1}{\epsilon_n - \epsilon_l} \right)$. In the small $k$ limit, we only keep the $k$-independent term and obtain the interaction Hamiltonian as follows,

$$\hat{H}_{\text{int}} = -\frac{e}{m} \mathbf{A} \cdot \hat{p}$$

(2)

For topological insulators (TIs), the bulk has inversion symmetry and will not contribute to the net HDPC. Therefore, we consider optical transitions between the bulk bands and the topological surface states. We use $\phi_{k,\eta}(z)$ and $\phi_{k,\eta'}(z)$ to denote the initial and the final states for an optical transition process. Thus, we have $H_0(z)\phi_{k,\eta}(z) = E_{k,\eta}\phi_{k,\eta}(z)$ and $H_0(z)\phi_{k,\eta'}(z) = E_{k,\eta'}\phi_{k,\eta'}(z)$. We further expand eigenstates of $H_0(z)$ in terms of basis $|n\rangle$ as $\phi_{k,\eta}(z) = \sum_n h_{\eta,n}(k) c_{\eta,n}(k)|n\rangle$. Thus, we have $|M|^2_{\eta\eta'} = \langle \phi_{k,\eta'} | H_{\text{int}} | \phi_{k,\eta} \rangle = -\frac{e}{m} \mathbf{A} \cdot \sum_{n,n',n''} h_{\eta,n}(k) c_{\eta',n'}(k) c_{\eta,n''}(k) \langle n | \hat{p} | n' \rangle$. By denoting $D_{\eta \eta'} = \frac{e}{m} \sum_{n,n',n''} d_{\eta,n}(k) c_{\eta',n'}(k) P_{nn'}$ with $P_{nn'} = \langle n | \hat{p} | n' \rangle$, the photocurrent can be rewritten
We learn that the bulk band eigenstates of Bi-chalcogenides in the double group where $M$ away from calculation, here we omit the unit/Pauli matrices in spin and orbital spaces, respectively. To simplify our on the basis of atomic orbitals (Bi, Se, Sb), $|\tau, p, z\rangle = \sqrt{\omega} \phi$, and $|\tau, p, z\rangle$ forms states with angular momentum $j_z = \pm \frac{3}{2}$, while $\Gamma_{4,5}^+$ form states with angular momentum $j_z = \pm \frac{1}{2}$. States with $j_z = \pm \frac{3}{2}$ in $\Gamma_{4,5}^+$, $\Gamma_{6}^+$ IrRep can be expanded in terms of orbitals and spins as $|\Lambda_\pm, \frac{3}{2}\rangle = |\Lambda_\pm, p_+, \uparrow\rangle$ and $|\Lambda_\pm, -\frac{3}{2}\rangle = |\Lambda_\pm, p_-, \uparrow\rangle$, where $\Lambda$ represents different combinations of atomic orbitals (Bi, Se, Sb), $|p_+\rangle = -\frac{1}{\sqrt{2}}(|p_x\rangle + i|p_y\rangle)$ and $|p_-\rangle = \frac{1}{\sqrt{2}}(|p_x\rangle - i|p_y\rangle)$. Furthermore, we express states in $\Gamma_{4,5}^+$ IrRep as $|\Lambda^\pm, \Gamma_{4,5}^+\rangle = \frac{1}{\sqrt{2}}(|\Lambda_\pm, \frac{3}{2}\rangle + |\Lambda_\pm, -\frac{3}{2}\rangle)$. For states in $\Gamma_{6}^+$ IrRep, we have $|\Lambda_\pm, \frac{1}{2}\rangle = u_\Lambda|\Lambda_\pm, p_+, \uparrow\rangle + v_\Lambda|\Lambda_\pm, p_-, \downarrow\rangle$ and $|\Lambda_\pm, -\frac{1}{2}\rangle = u_\Lambda^*|\Lambda_\pm, p_-, \downarrow\rangle + v_\Lambda^*|\Lambda_\pm, p_+, \uparrow\rangle$, where $|\Lambda_\pm, \frac{1}{2}\rangle$ is obtained from $|\Lambda_\pm, \frac{1}{2}\rangle$ by applying time reversal symmetry operation $T$. Here we have used $T|\Lambda_\pm\rangle = |\Lambda_\pm\rangle$, $T|\uparrow\rangle = |\downarrow\rangle$, $T|\downarrow\rangle = |\uparrow\rangle$, $T|p_+\rangle = |p_+\rangle$, $T|p_-\rangle = -|p_-\rangle$ and $T|p_-\rangle = -|p_+\rangle$.

The states near the Fermi level belong to $\Gamma_{6}^+$ IrRep, which are denoted as $|P_1^+, \uparrow\rangle$, $|P_1^+, \downarrow\rangle$, $|P_2^-, \uparrow\rangle$ and $|P_2^-, \downarrow\rangle$, respectively. These states contribute to the nontrivial topological property. The effective Hamiltonian constructed from both symmetry principles and $k \cdot p$ theory is written as

$$H_1 = (M_0 + M_1 k_z^2) \tau_z \otimes \sigma_0 + B_0 k_z \tau_y \otimes \sigma_0 + A_0 \tau_x \otimes (\sigma_x k_y - \sigma_y k_x) \quad (4)$$

on the basis $\Psi = (|P_1^+, \uparrow\rangle, |P_1^+, \downarrow\rangle, |P_2^-, \uparrow\rangle, |P_2^-, \downarrow\rangle)^T$, where $\sigma_{0,x,y,z}$ and $\tau_{0,x,y,z}$ are unit/Pauli matrices in spin and orbital spaces, respectively. To simplify our calculation, here we omit the $k_z^2$ and $k_y^2$ related terms without changing the physics we are considering. For bulk states within the photon energy range that stay far away from $|P_1^+, \sigma\rangle$ and $|P_2^-, \sigma\rangle$ states in energy, we assume that the Hamiltonian
takes a simple parabolic form.

\[ H_2 = (E_b + \frac{\hbar^2}{2m_b^*}k^2)\sigma_0 \]

(5)

with \( m_b^* \) denoting the effective mass of bulk bands.

After the presentation of model Hamiltonian, we start to discuss the interaction between the surface states and the bulk states. More explicitly, we need to demonstrate how to calculate \( P_{nn'} = \langle n | \hat{\mathbf{p}} | n' \rangle \). Possible bulk states \( |n\rangle \) include \( |P_{3,\sigma}\rangle \) and \( |P_{4,\sigma}\rangle \) states in the \( \Gamma_6^+ \) irreducible representation and \( |P_{5,\pm\frac{3}{2}}\rangle, |P_{6,\pm\frac{3}{2}}\rangle \) in the \( \Gamma_{4,5}^\pm \) IrRep, where \( P_{3,4,5,6} \) are notations for different possible bulk bands.

With the help of group theory and symmetry principle, we can figure out the nonzero interaction terms and also reduce the number of independent parameters. Recall that momentum operator \( \hat{p}_z \) belongs to \( \Gamma_1^- \) IrRep and \( \hat{p}_\pm \) belongs to \( \Gamma_3^- \) IrRep, where \( \hat{p}_\pm \equiv \frac{1}{2}(\hat{p}_x \pm \hat{p}_y) \). Furthermore, \( |P_{1,\sigma}\rangle \) belongs to \( \Gamma_6^- \) IrRep, \( |P_{2,\sigma}\rangle \) belongs to \( \Gamma_6^+ \) IrRep, \( |P_{5,\pm\frac{3}{2}}\rangle \) belong to \( \Gamma_{4,5}^+ \) IrRep and \( |P_{6,\pm\frac{3}{2}}\rangle \) belong to \( \Gamma_{4,5}^- \) IrRep. Moreover, the direct product of different representations is also useful, which is listed below.

\[
\begin{align*}
\Gamma_6^s \times \Gamma_6^s &= \Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ \\
\Gamma_6^s \times \Gamma_6^- &= \Gamma_1^- + \Gamma_2^- + \Gamma_3^- \\
\Gamma_6^+ \times \Gamma_{4,5}^+ &= \Gamma_3^\pm \\
\Gamma_6^- \times \Gamma_{4,5}^+ &= \Gamma_3^\mp 
\end{align*}
\]

where \( s = \pm \) denotes parity. Another useful tool we are using is the symmetry analysis. We denote the mirror symmetry operator as \( \mathcal{M}_x = \mathcal{I} \otimes \mathcal{C}_{2,x} \) with yz plane as its mirror plane and time reversal symmetry operators \( \mathcal{T} \), where \( \mathcal{I} \) is the inversion operator and \( \mathcal{C}_{2,x} \) is the two-fold rotational symmetry operator. Under the mirror and time reversal symmetry operations, the momentum operators transform as

\[
\begin{align*}
\mathcal{M}_x \hat{p}_z \mathcal{M}_x^{-1} &= \hat{p}_z \\
\mathcal{M}_x \hat{p}_+ \mathcal{M}_x^{-1} &= -\hat{p}_x + i\hat{p}_y = -\hat{p}_- \\
\mathcal{M}_x \hat{p}_- \mathcal{M}_x^{-1} &= -\hat{p}_x - i\hat{p}_y = -\hat{p}_+ \\
\mathcal{T} \hat{p}_z \mathcal{T}^{-1} &= -\hat{p}_z
\end{align*}
\]
\[ T\hat{p}_+ T^{-1} = -\hat{p}_x - (-i)(-\hat{p}_y) = -\hat{p}_- \]
\[ T\hat{p}_- T^{-1} = -\hat{p}_x + (-i)(\hat{p}_y) = -\hat{p}_+ \]

For bulk band states \(|P_{i}^{\pm}, \sigma \rangle \) under the mirror symmetry transformation,

\[
\mathcal{M}_x |P_{1,2,3,4,5,6}^{\pm} \rangle = i |P_{1,2,3,4,5,6}^{\pm} \rangle
\]
\[
\mathcal{M}_x |P_{1,2,3,4,5,6}^{\pm} \rangle = i |P_{1,2,3,4,5,6}^{\pm} \rangle
\]
\[
\mathcal{M}_x |P_{5,6}^{\pm} \rangle = i |P_{5,6}^{\pm} \rangle
\]
\[
\mathcal{M}_x |P_{5,6}^{\pm} \rangle = i |P_{5,6}^{\pm} \rangle
\]

where \( \mathcal{M}_x |P_{1,2,3,4,5,6}^{\pm} \rangle = |P_{1,2,3,4,5,6}^{\pm} \rangle \), \( \mathcal{M}_x |P_{1,2,3,4,5,6}^{\pm} \rangle = i |P_{1,2,3,4,5,6}^{\pm} \rangle \), \( \mathcal{M}_x |P_{5,6}^{\pm} \rangle = i |P_{5,6}^{\pm} \rangle \), \( \mathcal{M}_x |P_{5,6}^{\pm} \rangle = i |P_{5,6}^{\pm} \rangle \)

For bulk band states \(|P_{i}^{\pm}, \sigma \rangle \) under time reversal symmetry transformation, we have

\[
\mathcal{T}|P_{1,2,3,4,5,6}^{\pm} \rangle = |P_{1,2,3,4,5,6}^{\pm} \rangle
\]
\[
\mathcal{T}|P_{1,2,3,4,5,6}^{\pm} \rangle = -|P_{1,2,3,4,5,6}^{\pm} \rangle
\]
\[
\mathcal{T}|P_{5,6}^{\pm} \rangle = -|P_{5,6}^{\pm} \rangle
\]
\[
\mathcal{T}|P_{5,6}^{\pm} \rangle = -|P_{5,6}^{\pm} \rangle
\]

where \( \mathcal{T}|P_{1,2,3,4,5,6}^{\pm} \rangle = |P_{1,2,3,4,5,6}^{\pm} \rangle \), \( \mathcal{T}|\uparrow \rangle = |\downarrow \rangle \), \( \mathcal{T}|\downarrow \rangle = -|\uparrow \rangle \), \( \mathcal{T}|p_+ \rangle = |p_- \rangle \) and \( \mathcal{T}|p_- \rangle = -|p_+ \rangle \)

Now we are ready to calculate \( P_{nn'} = \langle n |\hat{p}| n' \rangle \).

\( |P_{3}^{+}, \sigma \rangle \) bulk states in \( \Gamma_{6}^{+} \) IrRep—Recall that \( |P_{3}^{+}, \sigma \rangle \) belongs to \( \Gamma_{6}^{+} \) IrRep, \( \hat{p}_z \)

belongs to \( \Gamma_{6}^{-} \) IrRep and \( \hat{p}_z \) belongs to \( \Gamma_{3}^{-} \) IrRep. According to \( \Gamma_{6}^{+} \times \Gamma_{6}^{+} = \Gamma_{1}^{+} + \Gamma_{2}^{+} + \Gamma_{3}^{+} \), we know that only \( |P_{2}^{-}, \sigma \rangle \) from the surface states make a contribution to \( P_{nn'} \).

Moreover, there are only two independent terms in \( \langle P_{2}^{-}, \sigma |\hat{p}| P_{3}^{+} \rangle, \sigma' \). They are \( \langle P_{2}^{-}, \uparrow |\hat{p}_z| P_{3}^{+}, \uparrow \rangle \) and \( \langle P_{2}^{-}, \uparrow |\hat{p}_z| P_{3}^{+}, \downarrow \rangle \). The others are either forbidden by the \( C_3 \)
symmetry or related through these two terms.

\[ \langle P_{2}^{-}, \uparrow |\hat{p}_z| P_{3}^{+}, \uparrow \rangle = Q_3 \]
\[ \langle P_2^-, \uparrow | \hat{p}_+ | P_3^+, \downarrow \rangle = P_3 \]

where \( Q_3 = u_{P_2}^* u_{P_3} \langle P_2^-, p_z, \uparrow | (-i\hbar \partial_z) | P_3^+, p_z, \uparrow \rangle + v_{P_2}^* v_{P_3} \langle P_2^-, p_+ \downarrow | (-i\hbar \partial_z) | P_3^+, p_+ \downarrow \rangle \) and \( P_3 = u_{P_2}^* v_{P_3} \langle P_2^-, p_z, \uparrow | (-i\hbar \partial_z + \hbar \partial_y) | P_3^+, p_z, \uparrow \rangle + v_{P_2}^* u_{P_3} \langle P_2^-, p_+ \downarrow | (-i\hbar \partial_z + \hbar \partial_y) | P_3^+, p_+ \downarrow \rangle \), which are material-dependent parameters.

The other two terms: \( \langle P_2^-, \downarrow | \hat{p}_z | P_3^+, \downarrow \rangle, \langle P_2^-, \downarrow | \hat{p}_- | P_3^+, \uparrow \rangle \) can be obtained by either time reversal symmetry or mirror symmetry. Under mirror symmetry, \( \langle P_2^-, \downarrow | \hat{p}_z | P_3^+, \downarrow \rangle = \langle P_2^-, \uparrow | \hat{p}_z | P_3^+, \uparrow \rangle = \langle P_2^-, \uparrow | (-i) \hat{p}_z | P_3^+, \uparrow \rangle = Q_3 \). On the other hand, under time reversal symmetry, \( \langle P_2^-, \downarrow | \hat{p}_z | P_3^+, \downarrow \rangle = \langle TP_2^-, \uparrow | \hat{p}_z | TP_3^+, \uparrow \rangle = -\langle TP_2^-, \uparrow | T(\hat{p}_z) | P_3^+, \uparrow \rangle = -\langle \hat{p}_z P_3^+, \uparrow | P_2^+, \uparrow \rangle = -Q_3 \), where the property of anti-unitary of \( T \), \( \langle T \alpha | T \beta \rangle = \langle \beta | \alpha \rangle \), is used. Thus, \( Q_3 = -Q_3^* \), which is purely imaginary. Similarly, one can obtain \( \langle P_2^-, \downarrow | \hat{p}_- | P_3^+, \uparrow \rangle = -P_3 \) and \( \langle P_2^-, \downarrow | \hat{p}_- | P_3^+, \uparrow \rangle = P_3^* \). Thus, \( P_3 = -P_3^* \), which is also purely imaginary. In summary, we have

\[
\langle P_2^-, \uparrow | \hat{p}_z | P_3^+, \uparrow \rangle = \langle P_2^-, \downarrow | \hat{p}_z | P_3^+, \downarrow \rangle = Q_3 = i \frac{m}{\hbar} B_3 \\
\langle P_2^-, \uparrow | \hat{p}_+ | P_3^+, \downarrow \rangle = \langle P_2^-, \downarrow | \hat{p}_- | P_3^+, \uparrow \rangle = P_3 = i \frac{m}{\hbar} A_3
\]

, where \( A_3 \) and \( B_3 \) are purely real. The term \( \frac{m}{\hbar} \) is added in order to get \( A_3 \) and \( B_3 \) with unit of \( eV \cdot A \). Moreover, \( \langle P_3^+, \sigma | \hat{p}_z | P_2^-, \sigma \rangle \) can be obtained as

\[
\langle P_3^+, \uparrow | \hat{p}_z | P_2^-, \uparrow \rangle = \langle P_2^-, \uparrow | \hat{p}_z | P_3^+, \uparrow \rangle = (-i) \frac{m}{\hbar} A_3 \\
\langle P_3^+, \downarrow | \hat{p}_- | P_2^-, \uparrow \rangle = \langle P_2^-, \uparrow | \hat{p}_+ | P_3^+, \downarrow \rangle = (-i) \frac{m}{\hbar} B_3 \\
\langle P_3^+, \downarrow | \hat{p}_z | P_2^-, \downarrow \rangle = \langle P_2^-, \downarrow | \hat{p}_z | P_3^+, \downarrow \rangle = i \frac{m}{\hbar} B_3 \\
\langle P_3^+, \uparrow | \hat{p}_+ | P_2^-, \downarrow \rangle = \langle P_2^-, \downarrow | \hat{p}_- | P_3^+, \uparrow \rangle = i \frac{m}{\hbar} A_3
\]

Thus, the zeroth order of the light-matter interaction Hamiltonian \( \hat{H}_{int}(P_3^+) = -\frac{e}{m} \mathbf{A} \cdot \hat{p} \) in the small \( k \) limit on the basis \( (|P_2^-, \uparrow\rangle, |P_2^-, \downarrow\rangle, |P_3^+, \uparrow\rangle, |P_3^+, \downarrow\rangle) \) is expressed as

\[
H_{int}(P_3^+) = \frac{e}{\hbar} (B_3 A_x \tau_y \otimes \sigma_0 + A_3 A_x \tau_x \otimes \sigma_y - A_3 A_y \tau_x \otimes \sigma_x)
\]

, where \( A_{x,y,z} \) are \( x, y \) and \( z \) component of vector potential.
\( |P_4^-, \sigma \) bulk states in \( \Gamma^0_6 \) IrRep \(-\) The derivation for the coupling between \( |P_4^-, \sigma \) states and surface states is the same as that for states \( |P_3^+, \sigma \rangle \), except that the nonzero coupling terms come from \( \langle P_4^+, \sigma | \hat{p} | P_4^-, \sigma \rangle \). Here, we define that

\[
\langle P_1^+, \uparrow | \hat{p}_z | P_4^-, \uparrow \rangle = \langle P_1^+, \downarrow | \hat{p}_z | P_4^-, \downarrow \rangle = \frac{m}{\hbar} B_4 \\
\langle P_1^+, \uparrow | \hat{p}_+ | P_4^-, \downarrow \rangle = -\langle P_1^+, \downarrow | \hat{p}_- | P_4^-, \uparrow \rangle = \frac{m}{\hbar} A_4 \\
\langle P_4^-, \uparrow | \hat{p}_z | P_1^+, \uparrow \rangle = \langle P_4^-, \downarrow | \hat{p}_z | P_1^+, \downarrow \rangle = -\frac{m}{\hbar} B_4 \\
\langle P_4^-, \uparrow | \hat{p}_+ | P_1^+, \downarrow \rangle = -\langle P_4^-, \downarrow | \hat{p}_- | P_1^+, \uparrow \rangle = \frac{m}{\hbar} A_4
\]

, where \( B_4 = \frac{\hbar}{m} v_{p_1}^* v_{p_1} \langle P_1^+, p_z, \uparrow | (-\hbar \partial_x) | P_4^-, p_z, \uparrow \rangle + \frac{\hbar}{m} v_{p_4}^* v_{p_4} \langle P_1^+, p_+, \downarrow | (-\hbar \partial_x) | P_4^-, p_+, \downarrow \rangle \) and \( A_4 = \frac{\hbar}{m} v_{p_1}^* v_{p_4} \langle P_1^+, p_z, \uparrow | (-\hbar \partial_x - i\hbar \partial_y) | P_4^-, p_+, \downarrow \rangle + \frac{\hbar}{m} v_{p_4}^* v_{p_1} \langle P_1^+, p_+, \downarrow | (-\hbar \partial_x - i\hbar \partial_y) | P_4^-, p_+, \downarrow \rangle \), which are material-dependent parameters.

Thus, the zeroth order of the light-matter interaction Hamiltonian \( \hat{H}_{\text{int}}(P_4^-) = -\frac{\hbar}{m} \mathbf{A} \cdot \hat{\mathbf{p}} \) in the small \( \mathbf{k} \) limit on the basis \( \{ |P_1^+, \uparrow \rangle, |P_1^+, \downarrow \rangle, |P_4^-, \uparrow \rangle, |P_4^-, \downarrow \rangle \} \) is expressed as

\[
H_{\text{int}}(P_4^-) = \frac{\mathcal{E}}{\hbar} (B_4 A_x \tau_y \otimes \sigma_0 + A_4 A_x \tau_x \otimes \sigma_y - A_4 A_y \tau_x \otimes \sigma_x)
\]  

(7)

\( |P_5^-, \sigma \) bulk states in \( \Gamma^4_5 \) IrRep \(-\) Recall that \( |P_5^-, \pm \frac{3}{2} \rangle \) belongs to \( \Gamma^4_5 \) IrRep and \( \hat{p}_\pm \) belongs to \( \Gamma^3_5 \) IrRep. According to \( \Gamma^5_5 \times \Gamma^4_5 = \Gamma^3_5 \), we know that only \( |P_1^+, \sigma \rangle \) components in the surface states contribute to the matrix element. Moreover, there are only two independent terms in \( \langle P_1^+, \sigma | \hat{p} | P_5^-, \pm \frac{3}{2} \rangle \): \( \langle P_1^+, \uparrow | \hat{p}_+ | P_5^-, \frac{3}{2} \rangle \) and \( \langle P_1^+, \uparrow | \hat{p}_- | P_5^-, -\frac{3}{2} \rangle \). The other terms are either forbidden by the \( C_3 \) rotational symmetry or related through these two terms. We assume

\[
\langle P_1^+, \uparrow | \hat{p}_- | P_5^-, \frac{3}{2} \rangle = Q_5 \\
\langle P_1^+, \uparrow | \hat{p}_- | P_5^-, -\frac{3}{2} \rangle = P_5
\]

, where \( Q_5 = u_{p_1}^* \langle P_1^+, p_z, \uparrow | (-i\hbar \partial_x - \hbar \partial_y) | P_5^-, p_+, \uparrow \rangle \) and \( P_5 = v_{p_1}^* \langle P_1^+, p_+, \downarrow | (-i\hbar \partial_x - \hbar \partial_y) | P_5^-, p_-, \downarrow \rangle \), which are material-dependent parameters. The other two terms, \( \langle P_1^+, \downarrow | \hat{p}_+ | P_5^-, -\frac{3}{2} \rangle, \langle P_1^+, \downarrow | \hat{p}_+ | P_5^-, -\frac{3}{2} \rangle \) can be obtained by either time reversal symmetry or mirror symmetry. For instance, \( \langle P_1^+, \downarrow | \hat{p}_+ | P_5^-, -\frac{3}{2} \rangle = \langle P_1^+, \downarrow | \mathcal{M}_x P_1^+, \downarrow | \mathcal{M}_x \hat{p}_+ \mathcal{M}_x^{-1} \mathcal{M}_x | P_5^-, -\frac{3}{2} \rangle = \langle P_1^+, \downarrow | \mathcal{M}_x \hat{p}_+ \mathcal{M}_x^{-1} | P_5^-, -\frac{3}{2} \rangle = \langle P_1^+, \uparrow \rangle \)
\(|(-i)(-\hat{p}_-)i|P_5^-, \frac{3}{2}\rangle = -Q_5\). On the other hand, \(|P_1^+, \downarrow \rangle, |\hat{\rho}_+|P_5^-, \frac{3}{2}\rangle = \langle TP_1^+, \uparrow |\hat{\rho}_+|(-1)^n \mathcal{T} P_5^-, \frac{3}{2}\rangle = \langle TP_1^+, \uparrow \mathcal{T}(\hat{\rho}_-|P_5^-, \frac{3}{2}\rangle) = \langle \hat{\rho}_- P_5^-, \frac{3}{2}|P_1^+, \uparrow \rangle = \langle P_5^-, \frac{3}{2}|\hat{\rho}_+|P_1^+, \uparrow \rangle = Q_5^n. Thus, \(Q_5 = -Q_5^n\), which is purely imaginary.

Similarly, one can obtain \(|P_1^+, \downarrow \hat{\rho}_+|P_5^-, \frac{3}{2}\rangle = -P_5\) and \(|P_1^+, \downarrow \hat{\rho}_+|P_5^-, \frac{3}{2}\rangle = -P_5^n\). Thus, \(P_5 = P_5^n\), which is also purely real. In summary, we have

\[
\langle P_1^+, \uparrow \hat{\rho}_-|P_5^-, \frac{3}{2}\rangle = -\langle P_1^+, \downarrow \hat{\rho}_+|P_5^-, \frac{3}{2}\rangle = \frac{m}{\hbar}B_5
\]

\[
\langle P_1^+, \uparrow \hat{\rho}_-|P_5^-, \frac{3}{2}\rangle = -\langle P_1^+, \downarrow \hat{\rho}_+|P_5^-, \frac{3}{2}\rangle = -\frac{m}{\hbar}B_5
\]

Thus, the zeroth order of the light-matter interaction Hamiltonian \(\hat{H}_{\text{int}}(P_5^-) = -\frac{e}{m}\mathbf{A} \cdot \hat{\mathbf{p}}\) in the small k limit on the basis \((|P_1^+, \uparrow\rangle, |P_1^+, \downarrow\rangle, |P_5^-, \frac{3}{2}\rangle, |P_5^-, \frac{3}{2}\rangle)^T\) is expressed as

\[
H_{\text{int}}(P_5^-) = \frac{e}{\hbar}(B_5 A_x \tau_y \otimes \sigma_z + B_5 A_y \tau_x \otimes \sigma_y + A_5 A_x \tau_y \otimes \sigma_y + A_5 A_y \tau_y \otimes \sigma_z) \quad (8)
\]

**|P_6^+, \sigma\rangle** bulk states in \(\Gamma_{4,5}^+\) IrRep – The derivation of coupling is the same as the case for \(|P_5^-, \sigma\rangle\) bulk states, except that the nonzero coupling terms come from \(|P_2^-, \sigma \hat{\mathbf{p}}|P_6^+, \sigma\rangle\). Similarly, we have

\[
\langle P_2^-, \uparrow \hat{\rho}_-|P_6^+, \frac{3}{2}\rangle = -\langle P_2^-, \downarrow \hat{\rho}_+|P_6^+, \frac{3}{2}\rangle = i\frac{m}{\hbar}B_6
\]

\[
\langle P_2^-, \uparrow \hat{\rho}_-|P_6^+, \frac{3}{2}\rangle = -\langle P_2^-, \downarrow \hat{\rho}_+|P_6^+, \frac{3}{2}\rangle = \frac{m}{\hbar}A_6
\]

\[
\langle P_6^+, \frac{3}{2}|\hat{\rho}_+|P_2^-, \uparrow \rangle = -\langle P_6^+, \frac{3}{2}|\hat{\rho}_-|P_2^-, \downarrow \rangle = -i\frac{m}{\hbar}B_6
\]

\[
\langle P_6^+, \frac{3}{2}|\hat{\rho}_+|P_2^-, \uparrow \rangle = -\langle P_6^+, \frac{3}{2}|\hat{\rho}_-|P_2^-, \downarrow \rangle = \frac{m}{\hbar}A_6
\]

, where \(i\frac{m}{\hbar}B_6 = u_{P_2}^*\langle P_2^-, \hat{p}_z, \uparrow \rangle\left((-i\hbar \partial_x - \hbar \partial_y)|P_6^+, \hat{p}_z, \uparrow \rangle\right)\) and \(\frac{m}{\hbar}A_6 = v_{P_2}^*\langle P_2^-, \hat{p}_z, \downarrow \rangle\left((-i\hbar \partial_x - \hbar \partial_y)|P_6^+, \hat{p}_z, \downarrow \rangle\right)\), which are material-dependent parameters. \(A_5 \) and \(B_5\) are purely real.
Thus, the zeroth order of the light-matter interaction Hamiltonian \( \hat{H}_{int}(P_6^+) = -\frac{e}{m} \mathbf{A} \cdot \hat{\mathbf{p}} \) in the small \( k \) limit on the basis \((|P_2^+, \uparrow\rangle, |P_2^-, \downarrow\rangle, |P_6^+ , \frac{3}{2}\rangle , |P_6^+ , -\frac{3}{2}\rangle)\) is expressed as

\[
H_{int}(P_6^+) = \frac{e}{\hbar} (B_6 A_x \sigma_y \otimes \sigma_z + B_6 A_y \sigma_x \otimes \sigma_0 + A_6 A_x \sigma_y \otimes \sigma_y + A_6 A_y \sigma_y \otimes \sigma_x ) \quad (.9)
\]

2 Derivation of optical transition matrix and photocurrent for Bi-chalcogenides

In the following section, we will derive the matrix element and photocurrent for each possible bulk band. We start the derivation with introducing the wavefunctions of surface states and bulk states for a thin film of Bi-chalcogenides.

At \( \Gamma \) point \( k_x = k_y = 0 \) in the momentum, one can solve the Hamiltonian for the topological insulators, as shown in Eq. .4 in \( z > 0 \) space by replacing \( k_z \to -i\partial_z \). The two states can be expressed as \( |\Psi_\sigma\rangle = \frac{f(z)}{\sqrt{2}} (|P_1^+ , \sigma \rangle + |P_2^- , \sigma \rangle) \), where \( f(z) \) is a layer-dependent parameter and \( \sigma \) denotes spin up or spin down. We can see that the states with opposite parities couple to each other because of the inversion symmetry breaking for the surface. By projecting the bulk Hamiltonian of Eq. .4 onto the subspace of these two states \( |\Psi_{s,z}\rangle = (|\Psi_\uparrow\rangle, |\Psi_\downarrow\rangle) \) with \( k_z \to -i\partial_z \), we arrive at the effective Hamiltonian of the surface states, which is written as

\[
H_s = A_0 (k_y \sigma_x - k_x \sigma_y) \quad (.10)
\]

where \( A_0 > 0 \). The velocity of surface states has an order of magnitude \( v = A_0 / \hbar \sim 10^5 m/s \). Furthermore, one can solve for the two eigenstates of the topological surface states, expressed as \( \phi_{s,k,\xi} = \frac{1}{\sqrt{2}} (i \xi e^{-i\theta_k}, 1)^T \) with eigenenergy \( E_{s,k,\xi} = A_0 \xi |k| \), where \( \xi = \pm 1 \) labels the upper(lower) Dirac cone with left-handed(right-handed) spin texture, and \( \theta_k = tan^{-1}(\frac{k_x}{k_y}) \). Concretely, we expand the eigenstates \( \phi_{s,k,\xi} \) on the basis \( \Psi_s(z) = (|P_1^+, \uparrow\rangle, |P_1^+, \downarrow\rangle, |P_2^+, \downarrow\rangle, |P_2^-, \downarrow\rangle)^T \), which is expressed as

\[
\phi_{s,k,\xi} = f(z) (i \xi e^{-i\theta_k}, 1, i \xi e^{-i\theta_k}, 1)^T \quad (.11)
\]

For the bulk states, one can rearrange the eigenstates with in-plane left-handed and right-handed spin texture due to the degeneracy of bulk states. Explicitly, the
rearranged bulk eigenstates are expressed as
\[ \phi_{b,k,\eta} = \frac{1}{\sqrt{2}}(i\eta e^{-i\theta_k}, 1)^T \]
on the basis \( \Psi_b(z) = g(z)(|A_1^+, \uparrow (\frac{3}{2})\rangle, |A_1^-, \downarrow (-\frac{3}{2})\rangle)^T \), where \( \eta = \pm 1 \) represents the in-plane left-handed and right-handed spin texture. Here we would like to mention that \( \xi \) and \( \eta \) always label surface states and bulk states, respectively.

2.1 \( P_3^+ \) bulk states

2.1.1 Optical transitions from valence bands to surface bands

Recall that the matrix element for optical transitions from valence bands to surface bands is \( |\mathcal{M}|^2_{\xi\eta} = |\mathbf{A} \cdot \mathbf{D}_{\xi\eta}|^2 \) where \( \mathbf{D}_{\xi\eta} = \frac{\epsilon}{m} \sum_{z,n,n'} d^{z}_{\xi}(k, z) d_{\eta}(k, z) c^{*}_{\xi, n}(k)c_{\eta, n'}(k) \mathbf{P}_{nn'} \).

We first calculate \( \mathbf{D}_{\xi\eta} \). Here the parameters are taken as \( d_{\xi} = \frac{1}{\sqrt{2}}f(z) \), \( d_{\eta} = g(z) \), \( c_{\xi, |P_2, \uparrow\rangle} = \frac{1}{\sqrt{2}}i\xi e^{-i\theta_k} \), \( c_{\eta, |P_2, \downarrow\rangle} = \frac{1}{\sqrt{2}}i\eta e^{-i\theta_k} \), and \( c_{\eta, |P_3, \downarrow\rangle} = \frac{1}{\sqrt{2}}i\eta e^{-i\theta_k} \). Thus, we have
\[
\mathbf{D}_{\xi\eta}(v \rightarrow s) = \frac{\epsilon}{m} \sum_{z} \frac{1}{\sqrt{2}} f^{*}(z)g(z)(c^{\ast}_{\xi, |P_2, \uparrow\rangle}c_{\eta, |P_3, \downarrow\rangle} i\frac{m}{\hbar} B_3 + c^{\ast}_{\xi, |P_2, \downarrow\rangle}c_{\eta, |P_3, \downarrow\rangle} i\frac{m}{\hbar} B_3) = \frac{ieF_3}{2\hbar} (\eta \xi B_3 + B_3),
\]
where \( F_3 = \sum_{z} \frac{1}{\sqrt{2}} f^{*}(z)g(z) \), which is independent of the momentum by using small \( k \) approximation. Similarly, \( \mathbf{D}_{\xi\eta}(v \rightarrow s) = \frac{\epsilon}{m} \sum_{z} \frac{1}{\sqrt{2}} f^{*}(z)g(z)(c^{\ast}_{\xi, |P_2, \uparrow\rangle}c_{\eta, |P_3, \downarrow\rangle} i\frac{m}{\hbar} A_3) = \frac{ieF_3}{2\hbar} (\xi e^{i\theta_k} A_3) \) and \( \mathbf{D}_{\xi\eta}(v \rightarrow s) = \frac{\epsilon}{m} \sum_{z} \frac{1}{\sqrt{2}} f^{*}(z)g(z)(c^{\ast}_{\xi, |P_2, \downarrow\rangle}c_{\eta, |P_3, \downarrow\rangle} (-i\frac{m}{\hbar} A_3)) = \frac{ieF_3}{2\hbar} (\eta e^{-i\theta_k} A_3) \). Concretely,
\[
\mathbf{D}_{\xi\eta}(v \rightarrow s) = \frac{ieF_3}{2\hbar} [(\eta \xi B_3 + B_3)\hat{e}_z + (-i\eta e^{-i\theta_k} A_3 - i\xi e^{i\theta_k} A_3)/\sqrt{2}\hat{e}_x] + (\eta e^{-i\theta_k} A_3 - \xi e^{i\theta_k} A_3)/\sqrt{2}\hat{e}_y \]

, where \( \mathbf{D}_{\xi\eta}(v \rightarrow s) = \frac{1}{\sqrt{2}}(\mathbf{D}^{x}_{\xi\eta} + i\mathbf{D}^{y}_{\xi\eta}) \) and \( \mathbf{D}^{+}_{\xi\eta}(v \rightarrow s) = \frac{1}{\sqrt{2}}(\mathbf{D}^{x}_{\xi\eta} - i\mathbf{D}^{y}_{\xi\eta}) \) are used.

We assume the incident light towards the surface of Bi-chalcogenides has polar angle \( \theta \) and azimuthal angle \( \gamma \). The wavevector \( \mathbf{q} \) can be expressed as \( \mathbf{q} = -q(sin(\theta)cos(\gamma), sin(\theta)sin(\gamma), cos(\theta)) \). Furthermore, we obtain the vector potential as \( \mathbf{A}(t) = \mathbf{A}_E e^{-i\omega t + i\mathbf{q}\cdot \mathbf{r}} (-isin(2\varphi)sin(\gamma) + (1-icos(2\varphi))cos(\theta)cos(\gamma), isin(2\varphi)cos(\gamma) + (1-icos(2\varphi))cos(\theta)sin(\gamma), -(1-icos(2\varphi))sin(\theta)) + c.c., \) where \( \mathbf{A}_E = \frac{F_0}{\omega} \) with \( E_0 \) as the magnitude of the applied electric field and \( \varphi \) is the angle between the fast axis and the initial linear polarization of the light. The first term describes the photon absorption process while the second term describes photon emission process. For our experimental setup, \( \gamma = \pi \) and \( \varphi = \frac{\pi}{4}, \frac{3\pi}{4} \) for left/right circularly polarized light.
Thus, for an incident light, $A_x = -(1 - i \cos(2\varphi)) \cos(\theta) A_E$, $A_y = -i \sin(2\varphi) A_E$ and $A_z = -(1 - i \cos(2\varphi)) \sin(\theta) A_E$.

Now, we can calculate the matrix element $|\mathcal{M}|_{\xi \eta}^2(v \rightarrow s)$.

$$
|\mathcal{M}|_{\xi \eta}^2(v \rightarrow s) = \frac{e^2 F_s^2 A_k^2}{4\hbar^2} |A_3^2 \cos^2(\theta)(1 + \xi\eta(1 + \cos^2(2\varphi)) \cos(2\theta_k)) + A_3^2 \sin^2(2\varphi)(1 - \xi\eta \cos(2\theta_k)) + B_3^2 \sin^2(\theta)(1 + \cos^2(2\varphi))(1 + \xi\eta)^2 + \sqrt{2} A_3 B_3 \sin(2\varphi) \sin(\theta) \eta(1 + \eta \xi^2 \sin(\theta_k)) |
$$

Since the velocity $v_{k,\eta}$ is odd in terms of $k$ in the momentum space, only terms in $|\mathcal{M}|_{\xi \eta}^2$ that are asymmetric with respect to $k$ contribute to nonzero photocurrent. Therefore, the asymmetric part of matrix element, denoted as $|\mathcal{M}|_{\xi \eta,a}^2$, is expressed as

$$
|\mathcal{M}|_{\xi \eta,a}^2(v \rightarrow s) = \Delta_{\delta,\eta} \sin(2\varphi) \sin(\theta) s \xi \delta_{\eta}
$$

where $\Delta_{\delta,\eta} = \sqrt{2}\frac{F_s^2 A_k^2}{\hbar^2} A_3 B_3$ in unit of $eV$, $\xi = \pm 1$ indicates upper/lower Dirac cone with left-handed/right-handed spin texture and $\eta = \pm 1$ indicates bulk eigenstates with left-handed/right-handed spin texture.

We can obtain the following conclusions from the above expression for the asymmetric part of the matrix element. 1. $|\mathcal{M}|_{\xi \eta,a}^2$ depends on the helicity of the light; 2. The magnitude of $|\mathcal{M}|_{\xi \eta,a}^2$ is proportional to $\sin(\theta)$; 3. The nontrivial contribution to $|\mathcal{M}|_{\xi \eta,a}^2$ comes from optical transitions between surface states and bulk states with the same in-pane spin ($\xi = \eta$); 4. $|\mathcal{M}|_{\xi \eta,a}^2$ depends on the Dirac cone index $\xi$. The asymmetric part of matrix element contributed from the upper Dirac cone is opposite from that for the lower Dirac cone at the same momentum $k$. 6. $|\mathcal{M}|_{\xi \eta,a}^2$ depends on the sign of $A_3 B_3$, which depend on the property of different bulk states; 7. The $|\mathcal{M}|_{\xi \eta,a}^2$ is zero along line $k_y = 0$.

Now let us start the derivation of photocurrent from the bulk states $\phi_{b,k,\eta}$ with

$$
\mathbf{J}(v \rightarrow s) = -\frac{2\pi}{\hbar} \sum_{k,\xi,\eta} (\tau_\xi v_{k,\xi} - \tau_\eta v_{k,\eta}) |\mathcal{M}|_{\xi \eta,a}^2 (f_{k,\eta}^0 - f_{k,\xi}^0) \delta(E_{k,\xi} - E_{k,\eta} - \hbar \omega)
$$

$$
= \mathbf{J}_s(v \rightarrow s) + \mathbf{J}_b(v \rightarrow s)
$$

where $\mathbf{J}_s(v \rightarrow s) = -\frac{2\pi}{\hbar} \sum_{k,\xi,\eta} v_{s,k,\xi} |\mathcal{M}|_{\xi \eta,a}^2 (f_{k,\eta}^0 - f_{k,\xi}^0) \delta(E_{k,\xi} - E_{k,\eta} - \hbar \omega)$ is the photocurrent contributed from the surface states and $\mathbf{J}_b(v \rightarrow s) = \frac{2\pi}{\hbar} \sum_{k,\xi,\eta} v_{b,k,\eta} |\mathcal{M}|_{\xi \eta,a}^2 (f_{k,\eta}^0 - f_{k,\xi}^0) \delta(E_{k,\xi} - E_{k,\eta} - \hbar \omega)$ is the photocurrent contributed from the bulk states, where $\tau_s$ and $\tau_v$ represent relaxation time for surface and bulk carriers,
respectively. Recall \( E_{s,k,\xi} = A_0 \xi |k| \) and \( E_{b,k,\xi} = E_b - M_v k^2 \) with \( M_v \equiv \frac{\hbar^2}{2m_c} \).

Therefore, \( v_{s,k,\xi} = \frac{\partial E_{s,k,\xi}}{\partial |k|} \frac{\partial |k|}{\partial k_x} \hat{e}_x + \frac{\partial E_{s,k,\xi}}{\partial k_y} \hat{e}_y = \frac{A_0}{\hbar} \xi \cos(\theta_k) \hat{e}_x + \frac{A_0}{\hbar} \xi \sin(\theta_k) \hat{e}_y \) and \( v_{b,k,\eta} = -\frac{2}{\hbar} M_v |k| \cos(\theta_k) \hat{e}_x - \frac{2}{\hbar} M_v |k| \sin(\theta_k) \hat{e}_y \). We then calculate \( \mathbf{J}_s \) and \( \mathbf{J}_b \) by substituting the matrix element with the expression derived above. After steps of mathematical calculation, we arrive at

\[
\mathbf{J}_s(E_F, v \to s) = -\frac{e^3 F_3^2 A_E^2 A_s A_3 B_3 \sin(2\varphi) \sin(\theta) \tau_s S_s^2}{16\sqrt{2\pi^2 \hbar^4 A_0 M_v}} \left[ A_0 P_c^2 - sgn(E_F) E_F^2 \right] \hat{e}_y
\]

Where \( E_F \) is the Fermi energy, \( k_c \) is the cutoff momentum, \( sgn(E_F) \) denotes the sign of \( E_F \) and \( S_s \) can be regarded as the size of sample. We also assume that the condition \( E_{k,\xi} - E_{k,\eta} - \hbar \omega = 0 \) can be always fulfilled and the temperature is \( T = 0 \text{K} \) during the derivation process. Here we have also used the density of states for Dirac-cone surface states \( g(E_\xi, \theta_k) = S_s g(k, \theta_k) \right| dE_\xi = S_s |\frac{dF_3}{4\pi^2 \xi E_F}|| \frac{S_s E_F}{4\pi^2 A_0^2} | \frac{dE_\xi}{4\pi^2 A_0^2} |

\[
\mathbf{J}_b(E_F, v \to s) = -\frac{e^3 F_3^2 A_E^2 A_s A_3 B_3 \sin(2\varphi) \sin(\theta) \tau_v S_s^2}{4\sqrt{2\pi^2 \hbar^4 A_0^2 \sqrt{M_v}}} (E_v + \hbar \omega - E_F)^{\frac{3}{2}} \left( \frac{4}{15} (E_v + \hbar \omega) + \frac{2}{5} E_F \right) \hat{e}_y
\]

One can easily check that the maximum of function \( f(x) = (a - x)^{\frac{3}{2}} \left( \frac{4}{15} a + \frac{2}{5} x \right) \) happens when \( x = 0 \). Thus, the magnitude of \( \mathbf{J}_b(E_F, v \to s) \) takes its maximum when \( E_F = 0 \). It decays as the Fermi level moves away from the Dirac point.

We can obtain the following conclusions from the above expression for the photocurrent. 1. Photocurrent can only exist along \( y \) direction; 2. The sign of the photocurrents originates from \( sgn(-A_3 B_3 \sin(2\varphi)) \) for both \( \mathbf{J}_s \) and \( \mathbf{J}_b; \) 3. The magnitude of photocurrent, which is proportional to \( \sin(\theta) \), depends on the polar angle of incident light; 4. Only optical transition between surface states and bulk states with the same in-plane spin texture make a nontrivial contribution to the photocurrent; 5. \( \mathbf{J}_b \) is zero if either the surface states are empty or the surface states are fully occupied. The magnitude of \( \mathbf{J}_b \) takes its maximum when the Fermi level is at the Dirac point.

### 2.1.2 Optical transitions from surface bands to conduction bands

The derivation of the matrix element and photocurrent is the same as before, except that 1, changing \( M_v \) to \( M_c \equiv \frac{\hbar^2}{2m_c} \); 2, removing the negative sign of the photocurrent since carriers with opposite charges are left behind in surface(conduction) bands.
Another thing we would like to emphasize is that in the derivation for photocurrent from surface band to conduction band, we cannot simply exchange index $\eta$ and $\xi$. Instead, we need to change $B_3$ to $-B_3$ besides exchanging $\eta$ and $\xi$. Here we keep the assumption that $\xi(\eta)$ denotes the surface(conduction) bands. Therefore, the asymmetric part of the matrix element is

$$|\mathcal{M}|_{\xi,a}^2(s \rightarrow c) = -\Delta_{3,M} \sin(2\varphi) \sin(\theta) \sin(\theta_k) \xi \delta_{\xi 0} \tag{16}$$

where $\Delta_{3,M} = \frac{\sqrt{2} e^2 F_2^2 A_3^2}{\hbar^2} A_3 B_3$

Similarly, we obtain the photocurrent contributed from surface and bulk states as

$$J_s(E_F, s \rightarrow c) = -\Pi_3, j \tau_s \left[ A_0^2 k_c^2 + \text{sgn}(E_F) E_F^2 \right] \hat{e}_y$$

$$J_b(E_F, s \rightarrow c) = -\frac{e^3 F_3^2 A_E^2 A_3 B_3 \sin(2\varphi) \sin(\theta) \tau_s S_2^2}{4 \sqrt{2} \pi^2 \hbar^4 A_3^2 \sqrt{M_c}} (E_F + \hbar \omega - E_c)^\frac{3}{2} \left( \frac{4}{15} (\hbar \omega - E_c) - \frac{2}{5} E_F \right) \hat{e}_y$$

where $\int_a^b x \sqrt{c + x} dx = \frac{2}{5} ((c + b)^{\frac{5}{2}} - (c + a)^{\frac{5}{2}}) - \frac{2}{3} ((c + b)^{\frac{3}{2}} - (c + a)^{\frac{3}{2}})$ is used during the derivation process. One can easily check that the maximum of function $f(x) = (a + x)^{\frac{3}{2}} (\frac{4}{15} a - \frac{2}{5} x)$ happens when $x = 0$. Thus, the magnitude of $J_b(E_F, v \rightarrow s)$ takes its maximum when $E_F = 0$. It decays as the Fermi level goes away from the Dirac point.

### 2.1.3 Total photocurrent as a function of the Fermi level

In this subsection, we calculate the total photocurrent by combining both contributions to the photocurrent from the above discussions.

$$J_s(E_F) = -\Pi_3, j \tau_s \left[ A_0^2 k_c^2 \left( \frac{1}{M_v} + \frac{1}{M_c} \right) - \text{sgn}(E_F) E_F^2 \left( \frac{1}{M_v} - \frac{1}{M_c} \right) \right] \hat{e}_y \tag{17}$$

, where $\Pi_3, j = \Delta_{3,M} \frac{e S_2^2 \sin(2\varphi) \sin(\theta)}{32 \pi^2 \hbar^2 A_0}$. From Eq. 17, we find that if $M_v = M_c$, the total photocurrent contributed from surface bands is independent on the Fermi level. However, the mass of hole is greater than the mass of electron in reality, i.e. $M_v < M_c$. Thus, the magnitude of $J_s(E_F)$ is greater when $E_F < 0$ and asymmetric about $E_F = 0$. 98
The velocity of bulk states now changes to
\[ \mathbf{J}_b(E_F) = -4\Pi_{3,4}\tau_e \frac{(E_{E_0} - E_F)^\frac{3}{2}(\frac{4}{15}\delta_{E_0} + \frac{2}{5}E_F)}{A_0\sqrt{M_v}} + \tau_c \frac{(E_F + \delta_{E_0})^\frac{3}{2}(\frac{4}{15}\delta_{E_0} - \frac{2}{5}E_F)}{A_0\sqrt{M_c}} \hat{e}_y, \quad (18) \]
where \( \delta_{E_0} = E_v + \hbar\omega = \hbar\omega - E_c \). From Eq. (18), we find that the magnitude of total photocurrent contributed from the bulk contribution \( \mathbf{J}_b(E_F) \) is maximized at \( E_F = 0 \) and symmetric about \( E_F = 0 \) when \( M_c = M_v \). \( \mathbf{J}_b(E_F) \) becomes asymmetric about \( E_F = 0 \) when \( M_c \neq M_v \).

### 2.1.4 Photocurrent from the Rashba effect

Since there is an external gate voltage applied experimentally to tune the Fermi level, the Rashba effect on the bulk states will play a role here. The Rashba Hamiltonian reads \( H_R = \alpha_R(k_y\sigma_x - k_x\sigma_y) \) on the basis \( \Psi_{P_3} = (|P_3^+,\uparrow\rangle,|P_3^+,-\uparrow\rangle)^T \), where the sign and magnitude of \( \alpha_R \) depend on the direction and strength of the external applied electric field. Moreover, \( \alpha_R \) is inversely related to the effective mass of bulk states. In this part, we only consider the Rashba effect on the conduction bands, since effective mass of electrons is much smaller than the effective mass of holes.

The modified eigenstates of conduction bands of \( \Psi_{P_3} \) can be obtained by solving \( H_c = (E_c + M_c k^2)\sigma_0 + \alpha_R(k_y\sigma_x - k_x\sigma_y) \). Denote \( \alpha_R = s_\alpha|\alpha_R| \) with \( s_\alpha = \pm 1 \). The eigenstate reads \( \phi_{R,c,k,\eta} = \frac{1}{\sqrt{2}}(i\eta s_\alpha e^{-i\theta_k},1)^T \) with eigenenergy \( E_\eta = E_c + M_c k^2 + \eta|\alpha_R k| \) and \( \eta = \pm 1 \). Similarly, one can obtain the asymmetric part of matrix element as

\[ |\mathcal{M}|^2_R,\eta_\xi_\alpha(s \rightarrow c) = -\Delta_{3,M} \sin(2\varphi) \sin(\theta) \sin(\theta_k) \xi_\delta_\eta_\xi_\alpha \quad (19) \]

The velocity of bulk states now changes to \( \mathbf{v}_{k,\eta} = (2M_c|k| + \eta|\alpha_R|)\cos(\theta_k)\hat{e}_x + (2M_c|k|\sin(\theta_k) + \eta|\alpha_R|)\hat{e}_y \). Similarly, the photocurrent for optical transitions from surface bands to conduction bands can be expressed as

\[ \mathbf{J}_{R,s}(E_F, s \rightarrow c) = -\Pi_{3,4} \frac{1}{A_0\sqrt{M_c}}[A_0^2 k_c^2 + \text{sgn}(E_F)E_F^2] \hat{e}_y \quad (20) \]

\[ \mathbf{J}_{R,b}(E_F, s \rightarrow c) = -\Pi_{3,4} \frac{1}{A_0\sqrt{M_c}}(E_F + \hbar\omega - E_c + \frac{\alpha_R^2}{4M_c})^2(\frac{4}{15}(\hbar\omega - E_c + \frac{\alpha_R^2}{4M_c}) - \frac{2}{5}E_F) \]

\[ + \frac{\alpha_R}{4A_0M_c}(A_0^2 k_c^2 - \text{sgn}(E_F)E_F^2)] \hat{e}_y \]

99
From the equations above, we find that the Rashba splitting on the conduction bands does not affect the photocurrent contributed by the surface states. However, it indeed influences the photocurrent contributed from the conduction bands with $J_{R, b, \text{extra}} \sim -\alpha_R (a_b^2 k_c^2 - sgn(E_F) E_F^2) \hat{e}_y$ and makes the photocurrent more asymmetric about $E_F = 0$.

### 2.2 Bulk states: $|P_4^-, \sigma\rangle$

The derivation of the transition matrix element and photocurrent for $|P_4^-, \sigma\rangle$ states is the same as that for states $|P_3^+, \sigma\rangle$, except that the nonzero interaction terms come from coupling $\langle P_4^1, \sigma | \hat{p} | P_4^- \rangle$. The above derivation can be applied here directly by just replacing $A_3, B_3$ with $A_4, B_4$.

### 2.3 Bulk states: $|P_5^-, \pm \frac{3}{2}\rangle$ and $|P_6^+, \pm \frac{3}{2}\rangle$

In this subsection, we will first consider the contribution to photocurrent for optical transitions from valence bands to surface bands for $|P_5^-, \pm \frac{3}{2}\rangle$. Recall that surface states $\phi_{s,k} = \frac{1}{\sqrt{2}} (i \xi e^{-i\theta_k}, 1)^T$ and bulk states $\phi_{b,k,\eta} = \frac{1}{\sqrt{2}} (i \eta e^{-i\theta_k}, 1)^T$, i.e. $d_\xi = \frac{1}{\sqrt{2}} f(z), d_\eta = g(z), c_{\xi, |P_1^+, \eta\rangle} = \frac{1}{\sqrt{2}} i \xi e^{-i\theta_k}, c_{\xi, |P_1^+, \eta\rangle} = \frac{1}{\sqrt{2}} i \xi e^{-i\theta_k}$, and $c_{\eta, |P_5^-, \frac{3}{2}\rangle} = \frac{1}{\sqrt{2}}$. Thus, we have

$$D_{\xi \eta}(v \to s) = -\frac{ieF_5}{2\hbar} \left[ ((1 - \xi \eta) B_5 + (\eta e^{-i\theta_k} + \xi e^{i\theta_k}) A_5) / \sqrt{2} \hat{e}_x + ((1 + \xi \eta) B_5 + (\eta e^{-i\theta_k} - \xi e^{i\theta_k}) A_5) / \sqrt{2} \hat{e}_y \right]$$

where $F_5 = \sum z \frac{1}{\sqrt{2}} f^*(z) g(z)$, which is independent of the momentum by using small $k$ approximation.

Recall that $A_x = -(1 - i \cos(2\varphi)) \cos(\theta) A_E, A_y = -i \sin(2\varphi) A_E$ and $A_z = -(1 - i \cos(2\varphi)) \sin(\theta) A_E$. Now, we are ready to calculate the matrix element $|\mathcal{M}|_{\xi \eta}^2$.

$$|\mathcal{M}|_{\xi \eta}^2(v \to s) = | - (1 - i \cos(2\varphi)) \cos(\theta) A_E D_{\xi \eta}^x - i \sin(2\varphi) A_E D_{\xi \eta}^y |^2$$

$$= \frac{e^2 F_5^2 A_b^2}{8\hbar^2} [ \cos^2(\theta) (1 - \xi \eta)^2 D_{\xi \eta}^x (1 + \cos^2(2\varphi)) + (1 + \eta \xi)^2 D_{\xi \eta}^y \sin^2(2\varphi) + 2 \cos^2(\theta) (1 + \eta \xi \cos(2\theta_k)) A_b^2 (1 + \cos^2(2\varphi)) + 2(1 - \eta \xi \cos(2\theta_k)) A_b^2 \sin^2(2\varphi) + 2 A_b^2 \eta \xi \sin(2\theta_k) \sin(2\varphi) ] - \frac{e^2 F_5^2 A_b^2}{\hbar^2} \eta \sin(4\varphi) \cos(\theta) A_5 B_5 \cos(\theta_k)$$
where \((1 - \eta \xi)(1 + \eta \xi) = 0\) is used. Therefore, the asymmetric part of matrix element is

\[
\left| \mathcal{M} \right|_{5, \xi \eta, a}^2 (v \rightarrow s) = -\frac{e^2 F_3^2 A_{E}^2}{\hbar^2} \eta \sin (4 \varphi) \cos (\theta) A_5 B_5 \cos (\theta_k)
\]

(22)

Though the asymmetric part of the transition matrix element exists, there is no net photocurrent contributed from \(|P_{-5}^\pm \pm \frac{3}{2}\rangle\) bulk states. The reason is that for a surface state with index \(\xi\), both degenerate bulk eigenstates with index \(\eta = \pm 1\) will contribute to the matrix element with opposite signs, leading to zero net photocurrent. Similarly, optical transitions from surface bands to conduction bands also result in zero net photocurrent. The conclusion of zero net photocurrent can be applied to optical transitions between surface bands and \(|P_{6}^+, \pm \frac{3}{2}\rangle\) states.

This conclusion verifies the result of circularly polarized galvanic effect from the symmetry principle, where the photocurrent constrained by the three-fold rotational symmetry \(C_3(z)\) and mirror symmetry \(M_x\) in Bi-chalcogenides is written as

\[
J_{\text{CPGE}} = i \gamma [(A_z A_x^* - A_x A_z^*)\hat{x} - (A_y A_z^* - A_z A_y^*)\hat{y}]
\]

(23)

where \(\gamma\) is a material-dependent parameter. Thus, one needs \(A_z\) term to play an essential role for nonzero photocurrent. From the above calculation, we know that \(D_z = 0\) for optical transitions between \(P_{-5}^- (P_{6}^+)\) states and surface states. Since the matrix element couples \(D_z\) and \(A_z\), \(A_z\) will not be included in the calculation of photocurrent. Thus, there is no photocurrent induced by optical transitions with \(P_{-5}^- (P_{6}^+)\) states involved.

### 3 Photocurrent from optical transitions between two Dirac-cone surface states

Since there appears a second Dirac-cone surface states above the first Dirac cone, we need to consider the contribution to the photocurrent between the two Dirac-cone surface states. The Hamiltonian of the second surface state can be written as

\[
H_{s2} = A_{s2}(k_y \sigma_x - k_x \sigma_y)
\]

(24)
Similarly, one can solve for the two eigenstates of the surface states, expressed as \( \phi_{s2, k, \eta} = \frac{1}{\sqrt{2}} (i \eta e^{-i \theta_k}, 1)^T \) with eigenenergy \( E_{s2, k, \eta} = A_{s2} |\eta| k \), where \( \eta = \pm 1 \) labels the upper/lower Dirac cone.

If velocities of two Dirac-cone surface states are different, i.e., \( A_0 = A_{s2} \) and the photon energy matches the energy difference of two surface states, we have the photocurrent

\[
J(s \rightarrow s_2) = -\frac{2 \pi e}{\hbar} \sum_{k, (\xi, \eta)} (\tau_2 v_{k, \eta} - \tau_s v_{k, \xi}) |\mathcal{M}|^2_{\xi, \eta} (f_{k, \xi}^0 - f_{k, \eta}^0) \delta(E_{k, \eta} - E_{k, \xi} - \hbar \omega)
\]

where \( \tau_s (\tau_{s2}) \) is the relaxation time for carriers of the (first) second Dirac-cone surface states, \( \xi (\eta) \) denotes the first and second Dirac-cone surface states. If the velocities of two Dirac cone surface states are different, i.e. \( A_0 \neq A_{s2} \), only states on a specific ring in the momentum space can match the photon energy we use. For such a case, the contribution to the net photocurrent would be much smaller than that for the previously discussed cases. Therefore, we only consider the situation with \( A_0 = A_{s2} \). The difference between \( \tau_s \) and \( \tau_{s2} \) plays an essential role for the nonzero photocurrent for such situations.

Recall that the first Dirac-cone surface states \( \phi_{s, k, \xi} = \frac{1}{\sqrt{2}} (i \xi e^{-i \theta_k}, 1)^T \) and the second Dirac-cone surface states \( \phi_{s2, k, \eta} = \frac{1}{\sqrt{2}} (i \eta e^{-i \theta_k}, 1)^T \), i.e. \( \Delta = \frac{1}{\sqrt{2}} f(z) \),

\[
d_\eta = \frac{1}{\sqrt{2}} f_2(z), c_{\eta, |P^+_1 \rangle} = \frac{1}{\sqrt{2}} (i \xi e^{-i \theta_k}, c_{\xi, |P^-_1 \rangle} = \frac{1}{\sqrt{2}} i \xi e^{-i \theta_k}, \xi, |P^-_2 \rangle = \frac{1}{\sqrt{2}}, c_{\eta, |P^+_3 \rangle} = \frac{1}{\sqrt{2}} i \eta e^{-i \theta_k}, c_{\eta, |P^-_4 \rangle} = \frac{1}{\sqrt{2}} \text{ and } c_{\eta, |P^+_4 \rangle} = \frac{1}{\sqrt{2}}.
\]

Here we assume the second Dirac-cone surface states originate from the \( |P^+_3, \sigma \rangle \) and \( |P^-_4, \sigma \rangle \) states. Furthermore, we can solve for \( \mathcal{D}_{\xi, \eta} \) as \( \mathcal{D}_{\xi, \eta} (s \rightarrow s_2) = \frac{e}{m} \sum_{z, n, n', n''} d_{\eta, n' \to n''}^*(\mathbf{k}, z) d_{\xi, n''}(\mathbf{k}) c_{\eta, n'}(\mathbf{k}) P^z_{nn'} = \frac{e}{m} \sum_{z} \frac{1}{\sqrt{2} f^*_{2}(z)} \frac{1}{\sqrt{2} f(z)} (c_{\eta, |P^+_1 \rangle}^* c_{\xi, |P^-_1 \rangle} (\xi e^{-i \theta_k} + i \eta e^{-i \theta_k} + \eta e^{-i \theta_k} + i \xi e^{-i \theta_k}) (\xi e^{-i \theta_k} + i \eta e^{-i \theta_k} + \eta e^{-i \theta_k} + i \xi e^{-i \theta_k})) = \frac{e^{F_{s+1}} \xi e^{i \theta_k} (A_3 + A_4)}{2} \) and \( \mathcal{D}_{\eta, \xi} (s \rightarrow s_2) = \frac{e}{m} \sum_{z, n, n', n''} d_{\eta, n' \to n''}^*(\mathbf{k}, z) d_{\xi, n'}(\mathbf{k}) c_{\eta, n''}(\mathbf{k}) P^z_{nn'} = \frac{e^{F_{s+1}} \eta e^{i \theta_k} (A_3 + A_4)}{2} \)

Thus, we have

\[
\mathcal{D}_{\xi, \eta} (s \rightarrow s_2) = -\frac{ie^{F_{s+1}}}{2} [(\eta \xi + 1)(B_3 + B_4) \hat{e}_z + (i \eta e^{-i \theta_k} + i \xi e^{i \theta_k})(A_3 + A_4) \sqrt{2} \hat{e}_x - (\eta e^{-i \theta_k} - \xi e^{i \theta_k})(A_3 + A_4) \sqrt{2} \hat{e}_y]
\]

102
where $D^x_{\xi\eta}(v \to s) = \frac{1}{\sqrt{2}}(D^x_{\xi\eta} + iD^y_{\xi\eta})$ and $D^y_{\xi\eta}(v \to s) = \frac{1}{\sqrt{2}}(D^x_{\xi\eta} - iD^y_{\xi\eta})$ are used. The asymmetric part of matrix element, $|\mathcal{M}_{\eta\xi}|_a^2$, can be further calculated and expressed as

$$|\mathcal{M}_{\eta\xi}|_a^2(s \to s_2) = -\Delta s_{2,M} \sin(2\varphi)\sin(\theta)\sin(\theta_k)\xi\delta_{\xi\eta}$$

(25)

where $\Delta s_{2,M} = \frac{\sqrt{2}\pi^2 F^2_{34} A^2_{44} (A_3 + A_4)(B_3 + B_4)}{\hbar^4}$ in unit of $eV$ and $\xi = \pm 1$ ($\eta = \pm 1$) indicates upper/lower Dirac cone with left-handed/right-handed spin texture for the first Dirac-cone surface states (the second Dirac-cone surface states).

Once the photon energy we use matches the energy difference of the two Dirac-cone surface states, We have

$$J(s \to s_2) = -\frac{2\sqrt{2}\pi^2 F^2_{34} A^2_{44} A_0(A_3 + A_4)(B_3 + B_4)\sin(2\varphi)\sin(\theta)}{\hbar^4} (\tau_{s2} - \tau_s)\hat{c}_y$$

$$- \sum_{k, (\xi, \eta)} \delta_{\xi\eta} \sin^2(\theta) \left( f^0_{k, \eta} - f^0_{k, \xi} \right) \delta(E_{k, \xi} - E_{k, \eta} - \hbar\omega)$$

$$= \frac{2\sqrt{2}\pi^2 F^2_{34} A^2_{44} A_0(A_3 + A_4)(B_3 + B_4)\sin(2\varphi)\sin(\theta)}{\hbar^4} (\tau_{s2} - \tau_s)\hat{c}_y \frac{S_{\eta\xi}}{4\pi^2} \times$$

$$\Theta(-E_F) \int_{-k_c}^{k_F} |k|dk \int_0^{2\pi} \sin^2(\theta_k)d\theta_k + \Theta(E_F) \int_{k_c}^{k_F} |k|dk \int_0^{2\pi} \sin^2(\theta_k)d\theta_k$$

$$+ \int_{-k_c}^{k_F} |k|dk \int_0^{2\pi} \sin^2(\theta_k)d\theta_k$$

$$= \frac{\pi^2 F^2_{34} A^2_{44} A_0(A_3 + A_4)(B_3 + B_4)\sin(2\varphi)\sin(\theta)}{2\sqrt{2}\pi A_0 \hbar^4} (\tau_{s2} - \tau_s) \left[ A^2_{0c} k_c^2 + \text{sgn}(E_F) E_F^2 \right] \hat{c}_y$$

where $\mathbf{v}_{s, k, \xi} = \frac{4n}{h} \xi \cos(\theta_k)\hat{c}_x + \frac{4n}{h} \xi \sin(\theta_k)\hat{c}_y$, $k_F$ is the Fermi momentum and $k_c$ is the cut-off momentum. We still assume that the condition $E_{k, \xi} - E_{k, \eta} - \hbar\omega = 0$ can be always fulfilled and the temperature is $T = 0$ K during the derivation process.

We find that optical transitions between two Dirac-cone surface states could also contribute to the photocurrent, which is proportional to the difference of relaxation times for carriers of the two surface states. From the derivation, we also find that as the Fermi level moves up from valence bands to conduction bands, the magnitude of photocurrent contributed by the optical transitions between the two Dirac-cone surface states increases. However, our experimental observation of the gate dependent photocurrent does not match with the photocurrent dependence on the Fermi level here. We learn that the helicity dependent photocurrent contributed by the optical transitions between the first and second surface states is not the major effect in our observation.
Bibliography


Vita
Yu Pan

Education
The Pennsylvania State University, University Park
Ph.D. in Physics August 2017
University of Science and Technology of China, Hefei, China
B.S. in Physics July 2010

Publications and Preprints

Honors and Awards
Ovshinsky Student Travel Award, American Physical Society 2017
Peter Eklund Lecturing Award, Department of Physics, Penn State 2017
APS Mid-Atlantic Student Travel Award, American Physical Society 2015
David H. Rank Memorial Physics Award, Penn State 2011
David C. Duncan Graduate Fellowship of Physics, Penn State 2010