Ultrafast spectroscopy studies of topological insulators and transparent conductive oxides

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Ultrafast Spectroscopy Studies of Topological Insulators and Transparent Conductive Oxides

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Ultrafast Spectroscopy Studies of Topological Insulators and Transparent Conductive Oxides

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Abstract

Ultrafast optical spectroscopy, which is based on the development of the femtosecond laser, is an excellent tool for studying the electronic and vibrational properties of many solid-state systems. In this thesis, ultrafast optical pump-optical probe (OPOP) technique and terahertz time-domain spectroscopy (THz-TDS) have been used to study topological insulators (TIs) and transparent conductive oxides (TCOs).

As a TI, $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ (BSTS) is studied by OPOP in my Ph.D. work. The dynamics of carriers and phonons in BSTS at temperature from 10-300 K are revealed. A fast relaxation process of carriers has been found, which is the relaxation of electrons from higher energy level to the bottom of conduction band. Such process could be described by the two-temperature model, which is based on the electron-phonon interaction. Moreover, the temperature-dependent behavior of coherent optical phonons could be explained by the anharmonic effect. Furthermore, the optical penetration depth is obtained from the study of coherent acoustic phonon. Meanwhile, the validity of two-temperature model in BSTS makes it a good tool to study similar materials.

THz-TDS studies of two TCOs, Ta-doped TiO_2 and amorphous In_2O_3 (a- In_2O_3), will be introduced in this thesis. (1) In the study Ta-doped TiO_2 , conductivities of three samples with different doping concentration from 10-300 K were obtained. According to the temperature-dependence of THz conductivity, the nature of carriers in Ta-doped TiO_2 is identified as interacting polaron gas, rather than non-interacting electrons. The electron-phonon interaction in these samples is found to be highly

dependent on the doping concentration. Furthermore, the results indicate that the high conductivity of Ta-doped TiO_2 does not just originate from the high carrier density, but also its low electron-phonon coupling. (2) In the research of a- In_2O_3 , the conductivities of three samples grown at different temperatures are obtained. According to the Drude model fitting of the conductivities, carrier density and mobility are obtained, which show good electronic performance that comparable with crystalline In_2O_3 . Moreover, the mobility and carrier density of a- In_2O_3 is highly dependent on the growth temperature. Finally, in a- In_2O_3 , the mobility obtained from AC measurement is found to be different from Hall effect (a DC measurement), which might come from its amorphous nature.

Contents

Acknowledgements	i
Abstract	iii
List of Figures	viii
1 Introduction	1
1.1 Motivation	1
1.2 Outline of the thesis	3
Bibliography	4
2 Experimental Techniques	7
2.1 Optical pump-optical probe technique	7
2.2 Terahertz time-domain spectroscopy	11
2.2.1 Terahertz generation and detection	13
2.2.2 Terahertz time-domain spectroscopy setup	18
2.3 Optical pump-terahertz probe technique	20
Bibliography	23
3 Data Collection and Analysis Methods	25
3.1 Data collection techniques	25
3.1.1 Lock-in amplifier based data collection	26
3.1.2 Data acquisition (DAQ) card based data collection	27
3.2 THz transmission spectroscopy	29
3.2.1 THz-TDS data analysis	31

3.2.2	Asymmetric window function	35
3.2.3	Physical models of conductivity	37
	Bibliography	43
4	Optical Pump-Optical Probe Studies of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$	45
4.1	Introduction	45
4.1.1	Topological insulator	45
4.1.2	New topological insulator BSTS	47
4.1.3	Thermoelectric properties	48
4.1.4	OPOP study of similar materials	50
4.2	Experimental information	51
4.3	Results and discussions	53
4.3.1	Transient reflectivity of BSTS	53
4.3.2	Carrier dynamics	56
4.3.3	Phonon dynamics	61
4.4	Conclusion	64
	Bibliography	65
5	Terahertz Conductivity of Ta-doped TiO_2: Interacting Polaron Gas	
	Model	71
5.1	Introduction	71
5.1.1	Applications of TiO_2	73
5.1.2	Ta-doped TiO_2	74
5.1.3	Polaron	76
5.2	Experimental information	77
5.3	Results and discussions	79
5.3.1	THz-TDS data	79
5.3.2	Interacting many-polaron gas theory	81
5.3.3	Analysis of conductivity	84
5.4	Conclusion	89

Bibliography	90
6 Terahertz Measurements of Amorphous In₂O₃ films	96
6.1 Introduction	96
6.1.1 Amorphous materials	96
6.1.2 Transparent amorphous semiconductors	97
6.1.3 Amorphous In ₂ O ₃	99
6.2 Experimental information	102
6.3 Results and discussions	103
6.3.1 THz-TDS data	103
6.3.2 Drude model fitting	104
6.3.3 Power law fitting	108
6.4 Conclusion	109
Bibliography	111
7 Conclusions & Future Work	114
7.1 Conclusions of this thesis	114
7.2 Future work	116
7.2.1 Interface of 2D materials and topological insulators	116
7.2.2 Fast scan OPTP system	120
Bibliography	122

List of Figures

2.1	The principle of pump-probe technique	7
2.2	Typical OPOP setup in experiments	8
2.3	Geometry of a pulse compressor which consists of two prisms.	9
2.4	Typical time-resolved reflection signal obtained by OPOP technique. .	11
2.5	Schematic graphs for phase-space filling and pump-induced absorption.	12
2.6	THz generation based on photoconductive antenna.	14
2.7	THz detection based on photoconductive antenna.	14
2.8	THz waveform and corresponding power spectrum of Tera-SED 10 from our measurement.	15
2.9	Schematic diagram of EO crystal based THz detection.	16
2.10	Response function of ZnTe based EO detection for THz radiation. . .	17
2.11	Optical path and photograph of TPS Spectra 3000	19
2.12	Schematic of knife-edge measurement.	19
2.13	The results of knife-edge measurement for our home-built THz-TDS setup.	20
2.14	THz-TDS signal without any sample.	21
2.15	OPTP setup.	22
3.1	Front panel of lock-in amplifier SR830.	26
3.2	The schematic of DAQ card based data collection system.	27
3.3	The schematic of DAQ card based THz-TDS/OPTP system.	28
3.4	The signal from lock-in based data collection and DAQ based data collection in OPTP experiments.	29

3.5	The schematic of sample holder for THz-TDS/OPTP.	30
3.6	The photo of our cryostat.	31
3.7	Transmittance of vac-vac for two sample holders with diameter 7 mm and 3.5 mm.	32
3.8	The process of THz-TDS data analysis.	32
3.9	An example of THz-TDS data analysis	33
3.10	Schema of the THz beam between source and detector with or without transmitting through thin film sample.	34
3.11	The process to construct an asymmetric window function according to the THz signal in time-domain.	36
3.12	Conductivity of Drude model.	39
3.13	Conductivity of Lorentz model.	40
3.14	Conductivity of Drude-Smith model	41
4.1	The band structure of normal insulators and topological insulators. .	46
4.2	Band structure of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ measured by ARPES.	47
4.3	Spectral weight of various Bi-based topological insulators at 5K. . . .	48
4.4	The values of ZT for some materials.	49
4.5	$\Delta R/R$ signal and A_{1g} coherent phonon of Bi_2Te_3	51
4.6	Schematic of the transient surface charge and spin response to pho- toexcitation and their characteristic time scales.	51
4.7	BSTS sample attached on sample holder with GE varnish.	52
4.8	Cryostat (Janis ST-500) used in my experiment.	53
4.9	Transient reflection ($\Delta R/R$) signal at time delay $t < 50$ ps for low fluence experiments.	54
4.10	Transient reflection ($\Delta R/R$) signal at time delay $t < 50$ ps for high fluence experiments. The signal at $t < 10$ ps is shown in inset. . . .	55
4.11	Fluence dependence and temperature dependence of relaxation time τ_{A1} obtained from low fluence experiments.	58
4.12	Specific heat of BSTS measured from PPMS.	60

4.13	The dephasing time and frequency of the coherent optical and acoustic phonon.	62
5.1	Crystal structure of rutile and anatase TiO_2	72
5.2	Band structure of anatase TiO_2 calculated from different methods. . .	73
5.3	The basic principle and related energy levels of DSSC.	75
5.4	UV-vis transmission spectra of pure and Ta-doped TiO_2 samples and blue shift of the optical bandgaps of anatase Ta-doped TiO_2	76
5.5	Schematic of polaron.	77
5.6	Three samples with different growth conditions on SLAO substrates. .	78
5.7	Vacuum to vacuum signal for testing THz-TDS system.	79
5.8	THz-TDS data of sample A	80
5.9	Real and imaginary conductivity of samples	81
5.10	$\chi(\omega)$ of sample A, B and C.	85
5.11	Fitting results of Eq. 5.12.	87
6.1	Comparison between crystal, polycrystal and amorphous material. . .	97
6.2	Schematic orbital drawing of electron pathway in crystalline and amorphous ionic oxide semiconductors.	98
6.3	Resistivity vs. carrier concentration of In_2O_3	100
6.4	Mobility and crystalline fraction of In_2O_3 at different deposition temperature.	101
6.5	Atomic structures of a-In-X-O, X = Zn, Ga, Sn, or Ge.	101
6.6	a- In_2O_3 films on z-cut quartz substrates.	102
6.7	THz-TDS signal of a- In_2O_3 samples.	103
6.8	Conductivities of three a- In_2O_3 thin films at room temperature. . . .	104
6.9	Plasma frequency ω_p and scattering rate γ of a- In_2O_3 thin film samples.	105
6.10	Carrier density n and mobility μ of a- In_2O_3 thin film samples. . . .	106
6.11	Low frequency conductivity of three samples vs. temperature.	109
7.1	Structure of 2D transition metal dichalcogenides materials.	117

7.2	Complex conductance of WS ₂ /SLG and SLG films at 15K.	119
7.3	Transient terahertz electric field $\Delta E/E$ of WSe ₂ samples from OPTP measurement.	120

Chapter 1

Introduction

In this chapter, the motivation of my thesis work will be introduced. The organization and contents of each chapter will be presented at the end of this chapter.

1.1 Motivation

As one of the most important engines of the development of human culture, physics supports the physical foundation of modern society. Recently, the breakthrough and development in condensed matter physics, such as the discovery of topological insulators (TIs), novel transparent conducting oxides (TCOs) and so on, could help people solve many urgent problems on the earth, such as energy and environment issues, bottlenecks of electronics (such as the failure of Moore's law). Therefore, to maximize the potential value of those materials, it is necessary to understand the properties of carriers, phonons and their mutual interactions, which could be identified by studying their transport properties or other fundamental processes in picosecond (ps) or sub-picosecond (sub-ps) timescale. Two kinds of materials will be described in this thesis. First, topological insulators, which are materials with gapped bulk but conducting surface state with topological protection, will be studied. Its special surface states are quite useful for spintronics, so the study of electrons at the surface of these materials is important [1]. Second, TCOs, which

are materials with high conductivity and transmission in visible light range [2], will be investigated. TCOs are excellent materials for transparent electrodes or thin film transistor (TFT) materials, as an enabling technology for the next generation of computing, communication, and identification devices [3, 4].

Ultrafast optical spectroscopy, which is based on the development of the femtosecond laser, is an excellent tool for studying the electronic and vibrational properties of many solid-state systems [5]. As one of the simplest but powerful ultrafast spectroscopy technique, optical pump-optical probe (OPOP) has proved to be useful to study topological insulators. The A_{1g} coherent phonon has been studied in some topological insulators [6–9]. However, the dynamics of carriers in TIs has not been fully explored with optical pump-probe technique. In this thesis, the ultrafast dynamics of carriers and phonons in a new topological insulator $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ is studied.

Terahertz time-domain spectroscopy (THz-TDS) is a useful technique to elucidate the fundamental optical properties of materials, from which the complex refractive index, conductivity and dielectric function of material could be obtained [10]. Compared to traditional infrared (IR) measurements, which can only detect the intensity of light (electric field), the phase of electric field in THz-TDS measurement could be obtained directly without using Kramers-Kronig relation, which makes the results more reliable. Therefore, it is a suitable tool to study the electronic properties of semiconductors [11], superconductors [12], TIs [13, 14], as well as TCOs. TCOs are materials that are both conductive and transparent in the visible light regime. It is very useful in many fields, especially in photonics and information technology [4]. The novel developments of TCOs are diverse: some unconventional TCOs, such as Ta- or Nb-doped TiO_2 [15, 16], or some modified traditional TCOs, such as amorphous indium based materials [17, 18], have been studied recently. In this thesis, Ta-doped TiO_2 is studied because of its good conductivity, novel conduction mechanism and potential applications [16]. In the research of amorphous In_2O_3 , the good conductivity and unusual mobility change at different growth temperatures of

this material is studied [19].

1.2 Outline of the thesis

This thesis studies the carrier and phonon dynamics in topological insulators, and the THz conductivity of transparent conductive oxides. The experimental technique I used is OPOP and THz-TDS. The thesis is organized as follows:

- Chapter 2. The basic principles of pump-probe technique, THz generation and detection are introduced.
- Chapter 3. Two data collection techniques — lock-in amplifier and data acquisition card (DAQ) are introduced. The data analysis method in THz-TDS is presented. Finally, some simple physical models include Drude model, Drude-Smith model, Lorentz model are introduced.
- Chapter 4. Ultrafast dynamics of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ topological insulator are measured by OPOP technique from low temperature to room temperature. The results show a fast relaxation process of carriers induced by electron-phonon interaction, which could be described by the two-temperature model. Moreover, coherent optical and acoustic phonons generated by pump pulse are observed.
- Chapter 5. Ta-doped TiO_2 films are studied by THz-TDS. The results show that the carriers in such material are polarons, and the interacting polaron gas theory is necessary to describe the carrier properties of the samples.
- Chapter 6. Amorphous In_2O_3 films are studied by THz-TDS, revealing the properties of the charge carriers. The relationship between defects and the electronic properties (conductivity, carrier density and mobility) in this material is discussed.
- Chapter 7. Main results of this thesis is summarized. The plan of my future work and related preliminary work are presented.

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Chapter 2

Experimental Techniques

In this chapter, the ultrafast spectroscopy techniques used in this thesis are described in detail. The chapter contains three parts: (1) the principle of basic optical pump-optical probe technique, (2) terahertz time-domain spectroscopy and (3) optical pump-terahertz probe spectroscopy.

2.1 Optical pump-optical probe technique

Figure 2.1: The principle of pump-probe technique: (1) sample is excited by pump pulse with frequency ω_1 (2) the probe beam with frequency ω_2 can probe the properties of excited sample at the time after Δt (pump-probe time delay).

Optical pump-optical probe (OPOP) is an ultrafast spectroscopy technique,

which is based on ultrafast lasers (usually pulse width $\tau_p \sim \text{sub-100 fs}$). It is suitable for studying the dynamics of carriers, phonons and other quasiparticles in materials [1].

The basic principle of OPOP is shown in Fig. 2.1. In the setup, two ultrafast laser pulses (pump, frequency ω_1 and probe, frequency ω_2) are focused on the sample with a time delay Δt between them. The sample was excited by the pump pulse, then the probe can detect the photoinduced change of sample's properties (i.e. reflection, transmission or absorption) at the time Δt after pump excitation [2].

Figure 2.2: Typical OPOP setup in experiments (the diagram was made by Dr. Chan La-O-Vorakiat, King Mongkut's University of Technology Thonburi). The power ratio of pump and probe at the front of cryostat is 10:1 and could be controlled by two neutral density filters (ND-filters, not shown in this figure).

A typical OPOP setup which is utilized in our experiments is shown in Fig. 2.2. The femtosecond laser pulse ($<100 \text{ fs}$) is split into pump and probe by a beamsplitter. A time delay Δt between pump and probe is controlled by the delay stage with range

of 0-1.2 ns and resolution of ~ 10 fs. The sample is mounted in the cryostat and could be cooled down to 5 K. Two lens are used to focus the laser beam on the sample. The positions of pump and probe pulses on the sample can be adjusted by XYZ positioners and spatially overlapped. Usually the probe beam intensity on the sample is much weaker than pump beam to avoid re-pumping the sample (usually the ratio between intensity of pump and probe is 10:1), and the spot size of probe should be smaller than pump to make sure the probed region is pumped uniformly.

In ultrafast optical spectroscopy experiments, the change of reflection/transmission/absorption of the sample after excitation by pump beam is usually small compared to the ambient noise, so it is necessary to utilize some methods to increase the signal-to-noise ratio (SNR). Several techniques usually applied are: (1) lock-in detection with pump beam modulated by a mechanical chopper or acousto-optic modulator (AOM); (2) the polarization of pump and probe should be perpendicular to each other, then a polarizer parallel to probe beam could minimize the detection of pump beam by the photodiode (Caution should be taken about the possible contribution of the repolarization process); (3) Anti-vibration devices, such as isolators between cryostat and vacuum pumps, should be installed. With the optimized SNR, the system could detect changes in reflection ($\Delta R/R$, defined in Eq. 2.1) of 10^{-6} .

Figure 2.3: Geometry of a pulse compressor which consists of two prisms. The green dashed line is mirror (only two prisms are used, and the dashed lines are the images in the mirror).

The temporal resolution of OPOP is limited by the pulse width τ_p , which could be determined by measuring the cross-correlation of the pump and probe pulses at the sample position. Usually τ_p at sample position is longer than that at the beginning of optical path, which is the result of group delay dispersion (GDD) of pulses at each optics. Ultrashort pulses will be broadened as the shorter wavelength components travel slower than the longer wavelength components. There are some methods to minimize GDD, such as replacing the normal mirrors in optical path with low GDD mirror, or building a double-prism pulse compressor which could compress the pulse directly. The optical path of a pulse compressor is shown in Fig. 2.3, in which the difference of optical length between light with different wavelength could compensate the GDD from other optical devices. Our lab employs the double-prism method to compress the pulses.

The signal obtained from OPOP experiments is defined as:

$$\frac{\Delta R}{R} = \frac{R(t_p) - R_0}{R_0}; \frac{\Delta T}{T} = \frac{T(t_p) - T_0}{T_0}, \quad (2.1)$$

where R_0 (T_0) is the reflection (transmission) before pump excitation, $R(t_p)$ [$T(t_p)$] is the reflection (transmission) at delay time t_p after the pump excitation.

Typical transient reflection signal obtained by OPOP is shown in Fig. 2.4. The signal could be separated to two processes – rise signal and relaxation signal: (1) the sample is excited by pump pulse at time zero ($t_p = 0$ ps), then $\Delta R/R$ rises within rise-time τ_r , which is typically ~ 100 fs; (2) after the peak, relaxation process(es) with decay time τ_r will take place [1].

The rising signal in $\Delta R/R$ before peak usually comes from the excitation or photo-generation of carriers [2], while the origins of relaxation processes are diverse, such as carrier recombination, dissociation of exciton, cooling down of carriers and so on. Usually the photoinduced change in reflectivity is caused by electronic excitations (carriers) and/or lattice excitations (phonons) [3]. As shown in Fig. 2.5, for carriers, there are two mechanisms that could change the sample's reflection: absorption from photoinduced carriers and phase-space filling (bleaching). First,

Figure 2.4: Typical time-resolved reflection signal obtained by OPOP technique. Taken from Ref. [1]

photoinduced carriers created by pump pulse absorb more photons, which could increase reflection and decrease transmission. Second, carriers generated by pump excitation occupy more final states in transition process, which could decrease transition probability (increase reflection). Lattice excitation can induce oscillatory signal in $\Delta R/R$ via several mechanisms [3]: (1) interference between reflected light from sample's surface and strain wave caused by pump excitation [4]; (2) multiple reflection of the strain wave [4]; (3) coherent lattice vibration [5].

2.2 Terahertz time-domain spectroscopy

Terahertz (THz, 10^{12} Hz) radiation is electromagnetic wave whose wavelength is between IR and microwave. Usually, THz range is defined as 0.1–10 THz, which corresponds to 0.41–41 meV. Compared with the bandgap of semiconductors, which is usually ~ 1 eV, the energy of THz radiation is very small, so it is suitable

Figure 2.5: Schematic graphs for (a) phase-space filling and (b) pump-induced absorption.

to study low-energy excitations. For example, excitons in Si, whose energy is ~ 15 meV corresponding to ~ 3.6 THz, could be observed by THz-TDS directly [6]. Furthermore, because THz radiation can penetrate many dielectric materials, it could be applied in imaging that detects the inner part of objects, with applications in security check and medical imaging.

In IR spectroscopy experiments, due to the time resolution of detection, only the intensity of light could be measured, while the phase information of the electromagnetic wave is neglected. However, to do further analysis, such as obtain the complex refractive index ($\tilde{n} = n + i\kappa$), Kramers-Kronig (K-K) relation must be used, which connects the real and imaginary part of any analytic function $\chi(\omega)$ in the upper half-plane according to Eq. 2.2 and Eq. 2.3:

$$\text{Re}[\chi(\omega)] = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\text{Im}[\chi(\omega')]}{\omega' - \omega} d\omega', \quad (2.2)$$

$$\text{Im}[\chi(\omega)] = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\text{Re}[\chi(\omega')]}{\omega' - \omega} d\omega', \quad (2.3)$$

where $\mathcal{P}$ represents for Cauchy principal value. In practical data analysis, the integral can only be calculated within a finite interval because of the limited frequency range of IR setup. Therefore, the results from K-K relation in IR spectroscopy

cannot be too accurate. Compared to IR spectroscopy, terahertz time-domain spectroscopy (THz-TDS) is a phase-sensitive technique, which could measure the magnitude and phase of THz electric field simultaneously. Therefore, complex refractive index of materials could be obtained from its THz transmission measurement without K-K relation, which is the greatest advantage of this technique.

2.2.1 Terahertz generation and detection

Because THz radiation is located at the edge of both infrared and microwave, it could not be generated and detected efficiently by traditional optical or electronic methods [7]. Fortunately, nonlinear optics which is based on ultrafast laser was found to be a good method for THz generation and detection. Typically, photoconductive antenna and electro-optic (EO) crystals are the most widely used approaches.

Photoconductive antenna based THz generation and detection Photoconductive antenna is a semiconductor-based device (Fig. 2.6). Two metal electrodes are fabricated on a semiconductor substrate whose carrier mobility should be high enough, to ensure the fast carrier response to the incident ultrafast laser pulses (~ 100 fs or sub-100 fs pulse width). In this device, laser pulse generated carriers (electrons and holes) will move to two electrodes under the external electric field, generating a transient current. Because of their opposite charge, electrons and holes will move in different directions, and creates polarizations in the semiconductor material, which subsequently generate THz pulse [8]. After a relatively long time (subpicosecond [9]), the carriers will recombine and the device will recover to its initial state. The relationship between the strength of electric field of the THz pulse (E_{THz}) and incident laser (E_{Laser}) is:

$$E_{\text{THz}} \propto E_{\text{Laser}}^2 \propto I_{\text{Laser}}, \quad (2.4)$$

which shows that the higher the incident laser power I_{Laser} , the stronger the THz output (within the damage threshold).

Figure 2.6: THz generation based on photoconductive antenna.

Figure 2.7: THz detection based on photoconductive antenna.

The principle of THz detection based on photoconductive antenna is almost the same as generation except for the lack of bias voltage (Fig. 2.7). In the detection part, there are two pulses – a laser pulse (named as sampling pulse/beam) and a THz

pulse. Similar to THz generation, electrons and holes will be generated by sampling pulse. The motion of photoinduced carriers and related current $I(t)$ between two electrodes could be modulated by the transient THz electric field. The current is $I(t) \propto E_{\text{THz}} \times h$, where h is the distance between two electrodes. Therefore, by measuring the current between two electrodes, the strength of transient electric field within the sampling pulse width (τ_p) could be detected [8]. Usually τ_p is smaller than 100 fs, which is much shorter than the length of THz pulse (~ 5 ps), so by controlling the time delay (t_s) between sampling and THz pulses, the whole THz waveform [$E(t_s)$] can be sampled. As an example, some parameters of a GaAs-based

Table 2.1: Some parameters of SED 10 photoconductive antenna

Bias voltage	AC 5 V + DC offset 5 V
Frequency of bias voltage	80 kHz
Laser power	120 mW
Laser repetition rate	250 kHz
Pulse width	70 fs

photoconductive antenna (Tera-SED 10) in our setup, is listed in Table 2.1. The THz waveform of THz pulse from Tera-SED 10 is in Fig. 2.8, which shows that the THz spectrum ranges from 0.1-2.5 THz.

Figure 2.8: THz waveform and corresponding power spectrum of Tera-SED 10 from our measurement.

Electro-optic (EO) crystals based THz generation and detection In EO crystal, optical rectification, which is a second-order nonlinear effect, could be utilized for THz generation [10]. In principle, it is a kind of difference frequency

generation (DFG). Because of relatively broad spectra of incident ultrafast laser pulse, DFG between different frequency components in EO crystal could generate a broadband THz pulse. Many EO crystals, such as ZnTe, GaSe and LiNbO₃ [8] could be used to generate THz radiation, but their application is limited by their phonon spectrum. In THz range, many EO crystals show strong THz absorption of phonons, which will decrease the output power and frequency range significantly.

Figure 2.9: Schematic diagram of EO crystal based THz detection. Taken from Ref. [11].

THz detection by EO crystal is based on a second-order nonlinear effect called Pockels effect, that is, the change of the refractive index of EO crystal under external electric field, changing or producing birefringence. The relationship between refractive index (n) and external electric field (E) is [12]:

$$n(E) = n_0 - \frac{1}{2}\xi n_0^3 E^2, \quad (2.5)$$

where ξ is Pockels coefficient. Because the value of ξ is different for the light with different polarizations in an anisotropic medium with the existence of Pockels effect [12], the polarization of incident light could be modulated by external electric field. Therefore, by measuring the polarization change of sampling beam in EO crystal under transient THz radiation, the strength of THz electric field could be obtained. As shown in Fig. 2.9, a femtosecond laser pulse (sampling pulse/beam) overlaps on a part of THz pulse. After the EO crystal, the polarization of sampling pulse could be modulated by the overlapped part of THz electric field. A $\lambda/4$ wave-

plate and a Wollaston prism are used to separate the sampling beam to two beam with different polarization directions. Finally, the polarization could be detected by the balanced detector. Similar to the method in photoconductive antenna based THz detection, by controlling the delay between sampling and THz pulse, the whole THz waveform could be sampled.

Figure 2.10: Response function of ZnTe based EO detection for THz radiation. Taken from Ref. [13].

The frequency window of the system is highly dependent on the pulse width of laser because of the DFG nature of THz generation in EO crystal. In principle, laser pulses with smaller pulse width could generate broader-bandwidth THz radiation [13]. However, because of the absorption in material, as well as dispersion which could break the phase matching condition, there is a limit of the bandwidth for a certain material [13]. In addition to the factors above, the thickness of the detection EO crystal could influence on the response spectrum of the detection system, as shown in Fig. 2.10. It is obvious that the bandwidth of thinner ZnTe is broader since there is less phase mismatch and energy loss by absorption. However, the

sensitivity of the signal detected from thinner EO crystal should be smaller [13] because of shorter overlap length for the interaction between sampling pulse and THz pulse during the propagation in crystal. In practical experiments, one should carefully consider the advantages and tradeoffs of using thick or thin EO crystals.

2.2.2 Terahertz time-domain spectroscopy setup

In my THz-TDS experiments, two setups are used: (1) A commercial THz-TDS spectrometer (TPS Spectra 3000) manufactured by TeraView (Fig. 2.11); (2) home-built THz-TDS spectrometer based on 1 kHz repetition rate Coherent Legend-Elite. THz generation and detection of TPS Spectra 3000 is based on photoconductive antenna, whose spectral range is 0.06–4 THz (2 cm^{-1} – 120 cm^{-1}) in principle. While in our home-built THz-TDS spectrometer, ZnTe crystals with 1 mm thickness are utilized as THz source and detection with spectral range up to ~ 3 THz (Fig. 2.10). However, considering some practical factors in real experiments, such as sample holder’s aperture, absorption of cryostat’s windows and substrate of sample, etc., the real spectral range is 0.3–2.7 THz for the two setups.

In principle, the samples’ size should be larger than THz beam to obtain valid signal. Usually, the beam diameter of THz radiation could be measured knife-edge method, in which a blade is applied to cut the beam, and block part of the cross section of the beam (Fig. 2.12). By changing the shaded area (or d in Fig. 2.12), the power of THz radiation as a function of d could be obtained, such as the curves in Fig. 2.13, which is the result from our home-built THz-TDS setup. Conventionally, we define the diameter of THz beam as 10%-90% of THz electric field intensity (dashed lines in Fig. 2.13), and from such definition, the THz diameter in our setup could be estimated as ~ 2.5 mm

Usually the signals we detected in experiments is the transmitted electric field of THz radiation through samples. Typical THz signal without sample from TPS spectra 3000 in time domain is shown in Fig. 2.14(a). By using fast Fourier transform (FFT), THz signal in frequency domain could be obtained (Fig. 2.14(b)). The signal

Figure 2.11: (a) Optical path and (b) photograph of TPS Spectra 3000. Taken from Ref. [14].

Figure 2.12: Schematic of knife-edge measurement. By changing d , the blade can cover different cross section of the beam.

is the average of 900 measurements which finished within 3 minutes. The fast data taking and high SNR makes this spectrometer very good for experiments.

Figure 2.13: The results of knife-edge measurement for our home-built THz-TDS setup. The dashed lines indicate the 10% and 19% of THz electric field intensity.

2.3 Optical pump-terahertz probe technique

As shown in Fig. 2.15, optical pump-THz probe (OPTP) is a combination of optical pump-probe technique and THz-TDS setups. Laser beam is split into two at BS2: optical pump and THz generation. Pump beam could excite the sample and change the dielectric function in THz regime. Then THz-TDS is applied to measure the properties of the excited sample at the delay time τ_{pump} after the pump. There are two detection modes of OPTP: 1D and 2D scan mode.

1D scan mode In 1D scan mode, the sampling-stage (“Detector Delay” in Fig. 2.15) is fixed to the position that allows the sampling pulse to overlap on the peak of THz pulse. The pump-stage (“Optical Pump Delay” in Fig. 2.15) scans to change the delay time between THz pulse and pump pulse. Then the pump-induced THz peak change, which is a function of pump-probe delay time t_p (similar to OPOP), could be obtained. However, this is a frequency-integrated method, so we cannot extract the frequency-dependent material parameters using this method.

Figure 2.14: THz-TDS signal without any sample: (a) electric field in time domain, (b) electric field in frequency domain after Fourier transform.

2D scan mode In 2D scan mode, both the stages for sampling and pump can move. During the 2D scan mode measurement, the stage for pump beam move to a certain delay time after the pump pulse excitation firstly, then the stage for sampling beam scans to obtain the whole THz waveform, which is the same as THz-TDS. Then the electric field $E(t_s; t_p)$ as a function of sampling delay time t_s at a certain pump-probe delay time t_p could be obtained. Finally, we can measure the THz-TDS signal of the sample after pump excitation at selected delay times, from which the frequency-dependent material parameters, such as complex conductivity $\tilde{\sigma}(\omega, t_p)$, as a function of pump-probe delay time, could be obtained.

Figure 2.15: OPTP setup: the black thinner optical path is for THz-TDS; the red thicker optical path is for optical pump. Taken from Ref. [2].

Compared to 1D scan mode, more information could be obtained from 2D scan measurement, but it is obvious that 2D scan mode is time consuming, because there are two moving stages in this mode. Therefore, choosing appropriate pump delay times for 2D scan mode is necessary. The pump delay times should be both representative for the properties of the excited sample and with the minimum number of data points. Usually, 1D scan measurement could be performed before 2D scan, which could help to decide the pump delay times.

OPTP is very suitable for studying semiconductors, [15], 2D materials [16], solar cell materials [17] and so on. For example, in the OPTP study of solar cell materials, the carrier density and mobility as functions of pump delay time, could be obtained (the method will be introduced in the next chapter). Then the recombination dynamics, diffusion length and some other important information of the sample for solar cell application, could be obtained.

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Chapter 3

Data Collection and Analysis

Methods

In this chapter, data collection and analysis methods in pump-probe and THz-TDS experiments will be introduced. It contains two parts: (1) high signal-to-ratio (SNR) data collection technique in pump-probe setup, (2) material properties extraction method in THz-TDS/TRTS experiments.

3.1 Data collection techniques

In my experiments, the strength of laser pulses are measured by the photodiode, which is a device that converts light to current/voltage signal. However, compared to the ambient noise, signals in pump-probe and THz-TDS experiments are usually very weak, so techniques that can improve signal-to-ratio (SNR) in my experiments is necessary. There are two techniques that could be utilized in ultrafast spectroscopy experiments – (1) lock-in amplifier and (2) data acquisition (DAQ) card based data collection systems.

3.1.1 Lock-in amplifier based data collection

Lock-in amplifier is able to extract a signal with a certain modulated frequency from strong noised background.

The noise reduction ability of lock-in amplifier is based on the orthogonality of sinusoidal functions, that is, the integral I of a product of two sinusoidal functions over a relatively large interval

$$I = \frac{1}{T} \int_t^{t+T} \sin(2\pi f_1 \tau) \sin(2\pi f_2 \tau) d\tau \quad (3.1)$$

is non-zero only if $f_1 = f_2$.

Fig. 3.1 shows the diagram of lock-in amplifier, in which there are two inputs: signal input (U_{in} , from photodiode) and reference input (whose frequency is f_{ref}). In the lock-in amplifier, the input signal will be multiplied by reference signal and integrated over a specified time. Finally, in U_{in} , only the component whose frequency is equal to f_{ref} can survive after the integration. Therefore, the lock-in amplifier can filter the noise and calculate the average value of the input signal during the integration time.

Figure 3.1: Front panel of lock-in amplifier SR830. Taken from official website of Stanford Research System (<http://www.thinksrs.com/products/SR810830.htm>)

In my experimental setup, the signal detected is modulated by a chopper (see in Fig. 2.2) whose frequency is set to f_{ref} . Such modulation signal is treated as

“Reference input”. Then the output of lock-in amplifier could be calculated by

$$U_{out} = \frac{1}{T} \int_t^{t+T} U_{in}(\tau) \sin(2\pi f_{ref}\tau + \phi) d\tau, \quad (3.2)$$

which is proportional to the signal we need. With a lock-in amplifier, the pump-probe setup is able to detect very weak signal in my ultrafast spectroscopy experiments ($\Delta R/R \sim 10^{-6}$ for OPOP).

3.1.2 Data acquisition (DAQ) card based data collection

Data acquisition card is a device that could measure the signal from sensors and transfer the data to computer. The basic functions of DAQ card are (1) analog-to-digital converter and (2) signal conditioning. Compared to traditional measurement systems, DAQ card based data collection system is more flexible and cost-effective.

Figure 3.2: The schematic of DAQ card based data collection system.

Fig. 3.2 shows a schematic of typical DAQ card based data collection system, where DAQ card works as a connector between computer and experimental instruments. Different from traditional analog-to-digital converter, there are programmable analog/digital outputs in DAQ card, which allow the users to control experimental instruments. Moreover, the multi-input and -output ports in DAQ card make it a multi-channel data collection system, which could collect data more

efficiently. Furthermore, the high time resolution of DAQ card makes it suitable for ultrafast optical spectroscopy, which could resolve the signal of each laser pulse.

In many ultrafast optical experiments, one of the main noise source is the laser power instability [1]. In DAQ based data collection setup, an additional photodiode is used for measuring the power of each laser pulse, that will help to minimize the noise from laser power instability [1].

As shown in Fig. 3.3, DAQ card could be applied in THz-TDS/OPTP experiments. The sampling signal comes from RF output of Ti:Sapphire laser, makes sure that the signals from balanced photodiode and photodiode of laser power detection for each laser pulse could be resolved. Meanwhile, other information during the data taking, such as the delay time (delay stage position) and pump on/off status (chopper on/off) could be measured and transferred to computer simultaneously.

Figure 3.3: The schematic of DAQ card based THz-TDS/OPTP system.

In practical experiments, the SNR of DAQ and lock-in based data collection, under the same experimental conditions, is comparable. An example (OPTP data) is shown in Fig. 3.4. It is obviously that the SNR of them are similar. However, to achieve good SNR, the integral time for lock-in amplifier should be significantly

Figure 3.4: The signal from lock-in based data collection and DAQ based data collection in OPTP experiments. Taken from Ref. [1].

longer than the modulation period ($1/f_{\text{ref}}$). Moreover, the response time of lock-in amplifier is larger hence slower than integral time when the signal changes. Therefore, compared to lock-in based data collection, DAQ card is more suitable for fast-scan system (see Chapter 7), where each laser/THz pulse can be recorded.

3.2 THz transmission spectroscopy

In THz-TDS/OPTP experiments on films, except for the sample's signal (E_{samp} , transmitted electric field of film+substrate), a reference signal (E_{ref}) is necessary, which is the transmitted electric field without sample (pure substrate, Fig. 3.5). With the data of sample and reference, transmission of the film could be obtained. Moreover, unwanted components in the signal, such as absorption and/or phase delay from substrate and windows, could be canceled in principle. Fig. 3.5 shows the diagram of sample holder for THz-TDS/OPTP experiments, in which the two

holes for sample and reference should be identical. The position of sample holder is controlled by a motorized Z-stage to move up and down, which could transfer sample and reference to the THz beam center with accuracy $\sim 2.5 \mu\text{m}$. In our THz-TDS setup, there is another stage to control the position of sample holder in x-y plane, which allows us to move the sample to the center of THz beam more accurately (Fig. 3.6).

Figure 3.5: The schematic of sample holder for THz-TDS/OPTP. There are two holes with identical diameter (3.5/7 mm) for sample and reference respectively. The sample holder was made of high thermal conductivity material, which is suitable for temperature controlling in cryostat. The whole sample holder could move up and down by a motorized stage to transfer the reference/sample to the position of THz radiation.

Before starting data measurements on samples, one needs to calibrate the setup. In such a calibration, the transmission of vacuum-to-vacuum (vac-vac) needs to be measured, where there are no sample and reference on the two holes of sample holder (sample = vacuum, reference = vacuum). The transmittance of vac-vac test is supposed to be unity and frequency-independent in principle, but there are always some errors in practical experiments, such as (1) the diameter difference of the two apertures, (2) line joining the centers of both apertures not parallel to the direction of travel of the z-stage, (3) THz beam not going through the centers of both apertures, (4) laser instability and so on. As an example, the transmittance signal of vac-vac for different sample holder in my setup is shown in Fig. 3.7. We clearly see that the sample holder with larger holes is better for real experiments.

Figure 3.6: The photo of our cryostat, which could be driven up and down by Z-stage, and move in x-y plane by X-Y-stage.

3.2.1 THz-TDS data analysis

A typical THz-TDS data analysis process is shown in Fig. 3.8. The raw data obtained from THz-TDS/OPTP is the electric field transmitted through the sample $[E_{\text{samp}}(t)]$ and reference $[E_{\text{ref}}(t)]$ in time-domain. After Fourier transform, $E_{\text{samp}}(\omega)$, $E_{\text{ref}}(\omega)$ and transmission $T(\omega) = E_{\text{samp}}(\omega)/E_{\text{ref}}(\omega)$ (in frequency-domain) can be calculated.

As an example, typical THz-TDS data which is sample and reference signal of Bi_2Se_3 film grown on c-cut sapphire is shown in Fig. 3.9(a). Because of the multi-reflections from backside of substrate, there are some echo signals (etalons, such as the one at ~ 10 ps and ~ 20 ps) after the main peak (at ~ 0 ps). The time difference between main peak and etalon (or between two etalons) is ~ 10 ps, which corresponds

Figure 3.7: Transmittance of vac-vac for two sample holders with diameter 7 mm (black solid curve) and 3.5 mm (red dashed curve). The average transmission is about 100% with fluctuation less than 2% and 0.2% for 7 mm and 3.5 mm respectively.

Figure 3.8: The process of THz-TDS data analysis.

to the thickness of sapphire substrate (0.5 mm). Before doing Fourier transform, etalons should be truncated [as shown in Fig. 3.9(a), data in the red dashed square].

Fourier transform could be performed on the time domain data with a certain window function. Because of the asymmetric shape of THz waveform in time

Figure 3.9: An example (Bi_2Se_3 thin film on c-cut sapphire) of THz-TDS data analysis: (a) truncate etalons in time-domain data (the red square is the data for Fourier transform), (b) electric field signal in frequency domain from (a) by Fourier transform, (c) transmission in frequency domain, (d) conductivity from material properties extraction process.

domain, asymmetric window function (see details in the next section) is necessary [2]. The frequency domain THz signal for sample and reference is shown in Fig. 3.9(b), in which the difference between them mainly results from absorption of Bi_2Se_3 thin film. Then the transmission could be obtained [Fig. 3.9(c)]. In general, dips in amplitude of transmittance usually suggest the presence of resonant absorptions, such as phonon [3] or exciton [4].

The last step is material properties extraction from transmission, which is based on a numerical methods [5]. To derive the expression of transmission of our sample-reference-setup, a schematic between THz source and detector is shown in Fig. 3.10. According to the figure, transmission as a function of frequency (ω) could be ob-

tained:

$$\tilde{T}(\omega) = \frac{\tilde{E}_{samp}(\omega)}{\tilde{E}_{ref}(\omega)} = \frac{2\tilde{n}(1 + \tilde{n}_{sub}) \exp\left[\frac{i\omega d(\tilde{n}-1)}{c}\right] \exp\left[\frac{-i\omega \Delta L(\tilde{n}_{sub}-1)}{c}\right]}{(1 + \tilde{n})(\tilde{n} + \tilde{n}_{sub}) + (\tilde{n} - 1)(\tilde{n}_{sub} - \tilde{n}) \exp\left[\frac{2i\omega d\tilde{n}}{c}\right]}, \quad (3.3)$$

where $\tilde{n}$ and $\tilde{n}_{sub}$ are refractive index for thin film and substrate respectively. $\Delta L = L_{sub2} - L_{sub1}$ represents for the thickness difference between two substrates for sample and reference.

Figure 3.10: Schema of the THz beam between source and detector with or without transmitting through thin film sample.

By using the numerical method introduced in Ref. [5], the frequency-dependent refractive index of thin film $\tilde{n}$ could be extracted. Then the complex dielectric function $[\tilde{\epsilon}(\omega)]$ and conductivity $[\tilde{\sigma}(\omega)]$ could be calculated from:

$$\tilde{\epsilon}(\omega) = \tilde{n}^2(\omega), \quad (3.4)$$

$$\tilde{\sigma}(\omega) = -i\epsilon_0\omega [\tilde{\epsilon}(\omega) - \epsilon_\infty], \quad (3.5)$$

where the ϵ_∞ is the high frequency dielectric constant (more details about ϵ_∞ will

be discussed later in this section).

The conductivity of Bi_2Se_3 obtained from THz-TDS is shown in Fig. 3.9(d). A dip in $\text{Re}[\tilde{\sigma}(\omega)]$ and an oscillation in $\text{Im}[\tilde{\sigma}(\omega)]$ at 1.9 THz comes from absorption of an optical phonon mode in Bi_2Se_3 , while the non-zero DC conductivity arises from the free carriers, which are consistent with the results in Ref. [6]. To explain the physics of those frequency-dependent parameters $[\tilde{\epsilon}(\omega), \tilde{\sigma}(\omega)]$, one need to apply appropriate physical models.

3.2.2 Asymmetric window function

In data analysis of THz-TDS, Fourier transform is utilized to convert the time-domain signal to frequency domain:

$$E(\omega) = \int_{-\infty}^{\infty} E(t) e^{-2\pi i \omega t} dt, \quad (3.6)$$

However, because of the limited time range (defined as t_1 — t_2) in practical THz-TDS data, we cannot obtain perfect frequency-domain signal, because in Eq. 3.6, the input function should be with infinity time range. Therefore, the signal in time-domain for Fourier transform is actually

$$E'(t) = E(t) \times w_r(t), \quad (3.7)$$

$$w_r(t) = \begin{cases} 0 & t < t_1 \text{ or } t > t_2, \\ 1 & t_1 < t < t_2, \end{cases} \quad (3.8)$$

where w_r is named as rectangular window.

It is obvious that the result from Fourier transform by multiplying a function, such as rectangular window w_r , is different from the real signal we need. Fortunately, we can replace w_r with an appropriate function w (window function) to minimize the deviation between the calculation result and the real signal. There are a lot of window functions, such as Hann window, Hamming window, Blackman-Harris

window, could be used in data processing method. Usually, those window functions are symmetric in time domain. However, because of the asymmetric shape of THz-TDS signal in time-domain, it is better to choose an asymmetric window function [2].

The asymmetric window function could be constructed according to the shape of THz electric field [2]: (1) separate the THz signal to two parts according to the position of the peak [Fig. 3.11(a)]; (2) generate two symmetric window functions according to each part [Fig. 3.11(b) and (c)]; (3) splice two half parts of symmetric window function [Fig. 3.11(d)].

Figure 3.11: The process to construct an asymmetric window function according to the THz signal in time-domain.

The symmetric function could be chosen as Blackman-Harris window or a sum of several Gaussian functions with different parameters [2], which have been proven to be excellent for THz data analysis [3, 7, 8].

3.2.3 Physical models of conductivity

To explain the features in $\tilde{\epsilon}(\omega)$ or $\sigma(\omega)$ in materials, physical models, such as Drude model, Lorentz model and Drude-Smith model, are frequently utilized.

Drude model In many conductive materials, the response of carriers (or photoinduced carriers in semiconductors), could be described by Drude model, which explains the transport properties of materials under an external electric field. There are several different derivations of Drude model, in which the classical model of charge transport is most intuitive [9]: the equation of motion for accelerated charges under the external electric field is

$$\frac{d^2\mathbf{r}}{dt^2} + \gamma \frac{d\mathbf{r}}{dt} = -\frac{e}{m}\mathbf{E}(t), \quad (3.9)$$

where e and m are the charge and effective mass of the carrier respectively, $\mathbf{r}$ is the ensemble average of the displacement of the charge carriers, γ denotes the scattering rate. Then the momentum $\mathbf{p}(t)$ of carriers under an AC electric field $\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$ could be obtained from Eq. 3.9:

$$\mathbf{p}(t) = \frac{d\mathbf{r}}{dt} = \mathbf{p}_0 \exp(-i\omega t), \quad (3.10)$$

$$\mathbf{p}_0 = \frac{e\mathbf{E}_0}{i\omega - \gamma}, \quad (3.11)$$

Then the current $\mathbf{J}$ is:

$$\mathbf{J}(t) = -\frac{ne\mathbf{p}(t)}{m} = \frac{ne^2}{m} \frac{1}{\gamma - i\omega} \mathbf{E}(t). \quad (3.12)$$

Here n is the carrier density. Considering the relationship between current and electric field:

$$\mathbf{J}(t) = \tilde{\sigma} \mathbf{E}(t), \quad (3.13)$$

the conductivity of Drude model $\tilde{\sigma}_D$ could be obtained:

$$\tilde{\sigma}_D(\omega) = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} \quad (3.14)$$

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m^*}}, \quad (3.15)$$

where ω_p is plasma frequency and ϵ_0 is the vacuum dielectric constant. Here the electron mass m is replaced by effective mass m^* because of the existence of periodic potential of lattice, electron-phonon coupling or some other interactions in the materials.

According to Eq. 3.5, dielectric function in Drude model is:

$$\tilde{\epsilon}_D(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (3.16)$$

A typical conductivity of Drude model is shown in Fig. 3.14. There are three obviously features: (1) at 0 THz, $\text{Re}(\sigma)$ is at maximum ($= \sigma_{DC}$), while $\text{Im}(\sigma)$ is zero, (2) $\text{Re}(\sigma)$ and $\text{Im}(\sigma)$ cross at $\omega = \gamma$, and equal to half σ_{DC} , (3) $\tilde{\sigma}$ tends to zero at higher frequency.

It should be noticed that the value of ϵ_∞ is exactly unity in theory. However, considering the limited frequency window ($0 - \omega_m$) of our measurement, the theoretical value of ϵ_∞ should be [10]:

$$\epsilon_\infty = 1 + \frac{2}{\pi} \int_{\omega_p}^{\infty} \frac{\text{Im}[\epsilon_2(\omega)]}{\omega} d\omega. \quad (3.17)$$

The exact value of ϵ_∞ is difficult to obtain from the calculation because of the lack of information of high-frequency conductivity. Therefore, ϵ_∞ is treated it as a fitting parameter in our data analysis process.

Figure 3.12: Conductivity of Drude model. The real and imaginary part of sigma cross at $\omega = \gamma$.

In the data analysis process, three parameters, ω_p , γ and ϵ_∞ , are extracted from the fitting of $\tilde{\sigma}(\omega)$ to the Drude model. Then we can obtain carrier density N according to Eq. 3.15 and mobility from the relation [9]:

$$\mu = \frac{e}{m^* \gamma}. \quad (3.18)$$

Lorentz model Resonant absorption process, such as absorption by phonons, excitons, plasmas and so on, could be described by Lorentz model [9]. In this model, dielectric function and conductivity could be written as:

$$\tilde{\epsilon}_L = \epsilon_\infty + \sum_j \frac{\omega_{pj}^2}{\omega_{0j}^2 - \omega^2 - i\omega\gamma_j}, \quad (3.19)$$

$$\tilde{\sigma}_L = \sum_j \frac{\epsilon_0 \omega_{pj}^2 \omega}{\omega\gamma_j + i(\omega_{0j}^2 - \omega^2)}, \quad (3.20)$$

where ω_{pj} , γ_{pj} and ω_{0j} represent for plasma frequency, scattering rate and resonance frequency of j -th Lorentz oscillator respectively.

Typical conductivity of Lorentz model is shown in Fig. 3.13. The two obvious features of a Lorentz model in conductivity are: (1) a peak in $\text{Re}(\tilde{\sigma})$ and a dip followed by a peak in $\text{Im}(\tilde{\sigma})$ at $\sim \omega_{0j}$, (2) both $\text{Re}(\tilde{\sigma})$ and $\text{Im}(\tilde{\sigma})$ tends to zero at very high and low frequency. At resonance frequency $\omega = \omega_0$, $\text{Re}(\tilde{\sigma})$ reaches its maximum and $\text{Im}(\tilde{\sigma}) = 0$. The full width at half maximum of conductivity $\tilde{\sigma}$ is determined by scattering rate γ . The resonance frequency usually represents for the frequency of phonon in phonon induced absorption in THz/IR range, or the energy gap in a semiconductor in visible/UV range.

Figure 3.13: Conductivity of Lorentz model (single oscillator, $j = 1$). Assume $\omega_0 = 5$ THz, $\gamma = 0.5$ THz.

Similar to Drude model, the four fitting parameters, ϵ_∞ , ω_{pj} , γ_{pj} and ω_{0j} , could be extracted from the fitting of $\sigma(\omega)$ to Lorentz model.

Drude-Smith model In nanomaterials or highly disordered materials, the conductivity cannot be well described by a pure Drude model [11, 12]. Smith [13] introduced backscattering and localization mechanism of carriers to explain the deviation between experimental results and Drude model. In this theory, conductivity could be described as:

$$\tilde{\sigma}_{DS} = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} \left(1 + \sum_j \frac{c_j}{(1 - i\omega/\gamma)^j} \right) \quad (3.21)$$

where c_j represents the fraction of electron's original velocity that is retained after j -th collision. The value of c_j is between -1 to 0 . Usually, the formula with $j = 1$ is good enough for most disordered samples.

Figure 3.14: Conductivity of Drude-Smith model (with the first order term $j = 1$ only). The curves are for different values of c_1

The conductivity spectra of Drude-Smith model for different c_1 are shown in Fig. 3.14. If $c = 0$, Drude-Smith model reduces to the simple Drude model. If $c_j = -1$, there is no DC conductivity ($\sigma_{DC} = 0$), and $\text{Re}(\tilde{\sigma})$ reaches its maximum

and $\text{Im}(\tilde{\sigma}) = 0$ at frequency $\omega = \gamma$. Another interesting feature is that $\text{Im}(\tilde{\sigma})$ could be negative at a certain frequency range if $c_j < -0.5$, which is frequently observed in disordered samples. In general, the more negative c_j is, the more localized the carriers are, and the greater the deviation from simple Drude model.

Combinations of models In a lot of materials, there might be responses from more than one mechanism. For example, there are both carriers and phonons in Bi_2Se_3 thin film [6] (see in Fig. 3.9), hence a pure Drude model or Lorentz model cannot describe its properties properly. Therefore, a linear combination of Drude and Lorentz model is necessary, which is named as Drude-Lorentz model with the expression:

$$\tilde{\sigma}_{DL} = \frac{\epsilon_0 \omega_p^2}{\gamma - i\omega} + \sum_j \frac{\epsilon_0 \omega_{pj}^2 \omega}{\omega \gamma_j + i(\omega_{0j}^2 - \omega^2)}, \quad (3.22)$$

The contribution from carriers in $\tilde{\sigma}(\omega)$ could be described by Drude term, while the peak at ~ 1.8 THz from phonon is explained by the Lorentz term.

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Chapter 4

Optical Pump-Optical Probe

Studies of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$

The ultrafast dynamics of carrier and phonon $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ (BSTS), a novel topological insulator, is studied by optical pump-optical probe technique from 10–300 K in this chapter. The temperature-dependent behavior of relaxation process of carriers has been explained by the two-temperature model (TTM). The phonon softening of coherent optical phonon were studied as well. We also obtained the optical penetration depth from the study of coherent acoustic phonon.

4.1 Introduction

BSTS is a V-VI semiconductor which is also a topological insulator [1]. Other TIs such as Bi_2Sb_3 and Bi_2Te_3 are good thermoelectric (TE) materials [2]. An ultrafast study (via OPOP) of BSTS will help us elucidate the carrier and phonon dynamics of TIs and TEs.

4.1.1 Topological insulator

Topological insulator has been a hotly-researched field in condensed matter physics recently due to their novel (topological) properties in electric structure, as well as for their potential applications in spintronics and quantum computation [4]. Because

Figure 4.1: The band structure of (a) normal insulators and (b) topological insulators. The shaded areas are the valance and conduction band. The black curves represent for the surface bands. Taken from Ref. [3].

of strong spin-orbit interaction and the presence of time-reversal symmetry in TIs, there are conducting surface states that cover the insulating bulk. Strong spin-orbit interaction induced non-trivial topology of wavefunction in momentum space leads to the existence of Dirac cones in bandgap, which is the origin of the special surface states. The comparison of normal 3D insulators and TIs is shown in Fig. 4.1. The Fermi level is located in the bandgap between conduction band (with symmetric wavefunction, “+”) and valance band (with antisymmetric wavefunction, “-”) in normal 3D insulators. Usually, at the surface of a 3D host, there are some surface states [see Fig.4.1(a)] [3], which cannot engage in conduction if Fermi level does not cross them. However, in some materials with strong spin-orbit coupling, the energy of antisymmetric states is higher than symmetric states in certain regions of momentum space, and then the surface states with different spins can cross over, which connect the valance and conduction band [Fig. 4.1(b) and (c)] [3]. Therefore, the Fermi level must be at the surface states, leading to a conducting surface. If the number of cross points is odd [Fig. 4.1(b)], backscattering of carriers on the surface cannot happen, because there is no mechanism (except for magnetic impurity or

magnetic field) to flip the spin and momentum of carriers simultaneously, which is different from Fig. 4.1(c) [3], where there is no need to flip spin in backscattering. The materials with such odd number of cross point(s) are called strong topological insulators.

4.1.2 New topological insulator BSTS

The potential applications of TIs are based on the properties their surface states, so the less (optical/electronic) response from the bulk, the better. However, unwanted bulk carriers in some TIs, such as Bi_2Se_3 , with relatively high bulk conductivity, are detrimental to their future application. Fortunately, topological insulators $\text{Bi}_2\text{Te}_2\text{Se}$ and $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ (BSTS), whose bulk conductivity is very low (1-10 Ωm), has been found recently [1]. In those materials, donors and accepters could compensate to each other, due to the precise control of the quantity ratio of each element, resulting in very low number of free carriers in the bulk, leading to very small bulk conductivity. The band structure of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ has been studied by angle-resolved photoemission spectroscopy (ARPES) [1], which shows that Fermi level could be shifted to Dirac point by controlling the ratio of each element.

Figure 4.2: Band structure of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ [(x, y) = (0, 1), (0.25, 1.15), (0.5, 1.3), (1, 2)] measured by ARPES. Taken from Ref. [1].

The surface-dominated conductivity in BSTS has been proved by transport [5]

and THz-TDS [6] measurement. In the transport experiment, the resistivity and Hall resistance measurements shows that the $\sim 99\%$ conductivity is contributed by the surface states in 200 nm thickness BSTS thin film. Meanwhile, ambipolar behavior and angle-dependent weak localization effect are observed, which confirmed the existence of topological surface states. THz-TDS experiment shows that the Drude spectral weight of BSTS (Fig. 4.3) is 1-2 orders magnitude smaller than in other Bi-based topological insulators, and similar to that of Bi_2Se_3 thin films, suggesting a significant contribution of the topological surface states to the conductivity of the BSTS sample. Due to its very insulating bulk compared to that in Bi_2Se_3 and Bi_2Te_3 , BSTS is therefore considered a very good TI.

Figure 4.3: Spectral weight of various Bi-based topological insulators at 5K. Taken from Ref. [6].

4.1.3 Thermoelectric properties

X_2Y_3 ($\text{X} = \text{Bi}, \text{Sb}$; $\text{Y} = \text{Se}, \text{Te}$) semiconductors are good thermoelectric materials, where electron-phonon coupling plays an important role in their thermoelectric performance [7]. The thermoelectric efficiency is defined by the figure of merit

$ZT = S^2 T \sigma / \kappa$ [8], where S is the Seebeck coefficient, σ and κ are electric and thermal conductivity respectively and T is temperature. X_2Y_3 semiconductors have relatively high ZT values as shown in Fig.4.4, and the material with one of the highest ZT reported is $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice [9] ($ZT = 2.4$, as comparison, the value of gold is 0.000162 [10]). Their good thermoelectric performance originates from low thermal conductivity [11]. In the study of $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice, some mechanisms, such as interface interaction of phonons [12, 13] and/or phonon localization [14], are suggested to be the microscopic explanations of the low thermal conductivity. Furthermore, OPOP study of $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice [15] observed: (1) phonon lifetime reduction (phonon lifetime in superlattice is shorter than in Bi_2Te_3 and Sb_2Te_3), suggesting weaker phonon-interface interactions and (2) relatively weaker electron-phonon coupling in this superlattice, suggesting the negative relationship between ZT and electron-phonon coupling.

Figure 4.4: The values of ZT for some materials. Taken from Ref. [2].

The thermal quality factor, B , which determines the optimized figure of merit, is inversely proportional to the deformation potential coefficient Ξ [7] in non-polar crystals. The deformation potential coefficient describes the change in energy of the electronic band with elastic deformation and thus describes the interaction between electrons and phonons [7]. Therefore, the study of electron-phonon interaction and related carrier dynamics in thermoelectric is important, which could help us search

for good thermoelectric materials.

4.1.4 OPOP study of similar materials

Pump-probe technique has been proved to be useful in the research of X_2Y_3 materials similar to BSTS. In some pump-probe researches, dynamics of coherent phonon has been studied [16–19], from which the dephasing time, amplitude and frequency of coherent phonons in Bi_2Se_3 , Sb_2Te_3 and Bi_2Te_3 are identified (Fig. 4.5). The $\Delta R/R$ signal of Bi_2Se_3 [19] after pump excitation shows the thermalization and energy relaxation of hot carriers occurs in the sub-ps timescale, whereas, the expansion of the differential reflection profile indicates that the ambipolar carrier diffusion coefficient and thermal diffusion coefficient are $\sim 500 \text{ cm}^2/\text{s}$ and $1.2 \text{ cm}^2/\text{s}$ respectively. Furthermore, the results of polarization-dependent OPOP measurements [16] confirm the spin-dependent optical transition selection rule in Sb_2Te_3 . In addition, the second harmonic generation from the surface states of Bi_2Se_3 has been studied both theoretically and experimentally [20]. Such method is applied to study the spin dynamics in bulk and surface of topological insulator as well (see in Fig. 4.6) [21], where the 800 nm circular polarized beam pump the and 400 nm linear polarized beam probe is utilized. From Fig. 4.6, we can see that the depolarization process happens within $\sim 0.2 \text{ ps}$, then the carrier relaxation happens.

However, the dynamics of carriers in those materials has not been fully explored (although the time scale of carrier relaxation is known, its mechanism is unknown), hence measurements, such as temperature-dependent OPOP experiments, should be performed to reveal the time-resolved carrier and phonon properties of such materials. In this chapter, the temperature-dependent ultrafast dynamics of carriers and phonons in a new TI $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ will be identified. The results of this work has been published in Appl. Phys. Lett. 104, 211906 (2014) [22].

Figure 4.5: (a) $\Delta R/R$ signal of Bi₂Te₃ with different pump fluence. (b) A_{1g} coherent phonon and its second harmonic effect found in Bi₂Te₃. Taken from Ref. [17].

Figure 4.6: Schematic of the transient surface charge and spin response to photoexcitation and their characteristic time scales. Taken from Ref. [21].

4.2 Experimental information

Sample preparation The sample is bulk Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2} (BSTS) single crystal, which was grown by Prof. Wang Lan from Royal Melbourne Institute of

Technology with modified Bridgman method. High purity (99.9999 %) Bi, Sb, Te and Se with molar ratio 1.5 : 0.5 : 1.8 : 1.2 was melted at 850°C in an evacuated quartz tube [5]. Some electronic properties have been studied in Ref. [5] and Ref. [6]. The thickness of this BSTS crystal is ~ 0.5 mm. The dimension of the sample could be seen in Fig. 4.7. In the experiment, BSTS sample was attached on a sample holder (copper plate) with GE varnish (see Fig. 4.7).

Figure 4.7: BSTS sample attached on sample holder with GE varnish.

Low temperature systems The sample with sample holder is placed in a cryostat (Janis ST-500, see Fig. 4.8) with a temperature controller (Lakeshore Model 331 Cryogenic Temperature Controller). The ST-500 cryostat can support 10^{-6} mbar vacuum, which is used for low temperature experiments. The low temperature environment is supported by a helium gas based Cryocooler (Janis, Cryogen Free Closed Cycle System). With those instruments, the temperature of the sample could be cooled down to 10 K with fluctuation less than 0.1 K.

Figure 4.8: Cryostat (Janis ST-500) used in my experiment.

OPOP setups Optical pump – optical probe measurements on BSTS were performed with two setups based on two lasers with different fluence (repetition rate). The optical path of these two setups are similar to Fig. 2.2. The fluence of pump and probe beam on the sample could be adjusted by ND-filters continuously. The low fluence setup is based on an oscillator (KMLabs Griffin), which is a 80 MHz, 800 nm output laser. Its pulse energy is $\sim$ nJ. The pump and probe beam were focused on the sample with diameter 60 μ m and 30 μ m respectively. Therefore, the fluence on BSTS sample is $\sim$ μ J/cm². The high fluence setup is based on an amplifier (Coherent RegA), which is a 250 kHz, 800 nm output laser. Its pulse energy is $\sim$ μ J. The diameters of pump and probe beam focused on the sample are 50 μ m and 25 μ m respectively. So the fluence on BSTS sample is $\sim$ mJ/cm².

4.3 Results and discussions

4.3.1 Transient reflectivity of BSTS

Photoinduced change in reflection ($\Delta R/R$) as functions of pump–probe time delay at selected temperatures are shown in Fig. 4.9 and Fig. 4.10 for low and high-fluence experiments respectively. It is obvious that the SNR of high fluence signals is better

than low fluence. Therefore, high fluence experimental results is more suitable to study some small features, such as the high frequency oscillations in $\Delta R/R$ (we will discuss it later).

Figure 4.9: Transient reflection ($\Delta R/R$) signal at time delay $t < 50$ ps for low fluence experiments. The red lines are the fitting curves from Eq. 4.1 The arrows indicate the first peak's position of low frequency oscillation signal (at ~ 15 ps). Taken from Ref. [22].

In low-fluence experiments (Fig. 4.9), the data shows a fast rising signal in $\Delta R/R$ with rise time about 200 fs, which results from the excitation of carriers as discussed in Chapter 2. The following fast decay and oscillatory processes occur after the peak. With further analysis, two oscillatory signals with different frequencies could be obtained. The high frequency part is relatively weak, while the low frequency

Figure 4.10: Transient reflection ($\Delta R/R$) signal at time delay $t < 50$ ps for high fluence experiments. The signal at $t < 10$ ps is shown in inset. The red lines are the fitting curves from Eq. 4.1. Taken from Ref. [22].

signal could be observed clearly. One peak of low frequency oscillation is at ~ 15 ps (indicated by arrows in Fig. 4.9), which has been reported in similar material (Bi_2Se_3 Ref. [23]). In larger time scale range, another nanosecond scale decay process in $\Delta R/R$ could be observed.

The high fluence data shows similar features as the one from low fluence experiments – two decay processes combined with high and low frequency oscillations could be observed (Fig. 4.10). The difference is that the high frequency oscillation is clearer. Therefore, the high fluence data is more suitable for study the oscillatory

signals.

Considering two decay processes and oscillations, the relaxation signal after the first peak could be fitted by the expression:

$$\frac{\Delta R}{R} = \sum_{i=1,2} A_i \exp\left(-\frac{t-t_0}{\tau_{Ai}}\right) + \sum_{j=1,2} B_j \exp\left(-\frac{t-t_0}{\tau_{Bj}}\right) \sin(2\pi f_j t + \phi_j) + C. \quad (4.1)$$

Here A_i and τ_{Ai} denote the amplitude and relaxation time of fast and slow decay process respectively. B_j , τ_{Bj} and ϕ_j represent for the amplitude, dephasing time and phase of the high and low frequency oscillatory signals. C is a constant. The red lines in Fig. 4.9 and 4.10 are the fitting curves according to Eq. 4.1, which shows very good fitting quality.

4.3.2 Carrier dynamics

The two decay components on $\Delta R/R$ are the results of two carrier relaxation processes. Here we focused on the fast relaxation ($\tau_{A1} \sim 1$ ps) process which is attributed to electron-phonon interaction. Another relaxation process with much longer lifetime is attributed to the diffusion of carriers out of the excitation volume. ($\tau_{A2} > 1$ ns)

Before we start the discussion of carrier dynamics, some information or assumption should be clarified: (1) According to previous transport experiments [5, 24], we can obtain the carrier density of bulk ($n_b = 2.3 \times 10^{16} \text{ cm}^{-3}$) and surface ($n_s = 4.0 \times 10^{12} \text{ cm}^{-2}$) of BSTS. Hence the number of carriers in the photoexcited volume [$\sim 50 \mu\text{m}$ diameter, 27 nm penetration depth (derived later), ~ 2 nm thickness of surface layer [25]] could be calculated as 7.9×10^7 and 1.1×10^6 for surface layer and bulk part respectively. Furthermore, with the consideration of sample reflectance, the number of photons absorbed by the sample per pump pulse in low fluence experiments is 5.7×10^7 (for $1.3 \mu\text{J}/\text{cm}^2$). Therefore, almost all the photon in pump pulse was absorbed by the carriers from surface rather than the bulk. (2) According to the results from time- and angle-resolved photoemission spectroscopy

(tr-ARPES) experiment [26], the fast decay in $\Delta R/R$ corresponds to the relaxation process of photoexcited electrons from high energy level to the bottom of conduction band, which is dominated by electron-phonon coupling. (3) We assume that in our BSTS, the carrier thermalization process happens within ~ 200 fs after pump, which is true for a similar material, Bi_2Se_3 [27, 28].

The relaxation time (τ_{A1}) of fast decay component in $\Delta R/R$ is consistent with the timescale of carrier relaxation process mediated by electron-phonon interaction in metals, which is from sub-picosecond to picosecond [29]. From our experimental data, with the pump fluence or temperature increasing, τ_{A1} increases accordingly [Fig. 4.11 (a)]. Such dependence could be explained by two-temperature model (TTM) [29, 30], which is suitable to describe the dynamics of free carriers in metals. Considering that: (1) photon absorption in photoexcited volume is dominated by the carriers on the surface and (2) as a topological insulator, BSTS contains a metallic surface [24], TTM should be applicable for our present scenario.

In two-temperature model, the sample is treated as a combination of two subsystems – electron and lattice. Immediately after photoexcitation, the temperature of electron system will increase because of photon absorption, while the temperature of lattice system remains unchanged. Temperature difference between two systems will lead to energy transfer. The whole process could be described by two coupled heat equations: [29]

$$C_e \frac{dT_e}{dt} = \nabla \cdot (\kappa \nabla T_e) - H(T_e, T_l) + P(t), \quad (4.2)$$

$$C_l \frac{dT_l}{dt} = H(T_e, T_l), \quad (4.3)$$

where T_i and C_i ($i = e, l$ for electron and lattice) are temperature and specific heat for the subsystem. $P(t)$ represents the amount of pump pulse power that is initially in the photoexcited volume. $H(T_e, T_l)$ is the energy transfer rate between electron and lattice subsystems. The term $\nabla \cdot (\kappa \nabla T_e)$ describes the energy dissipation from electron diffusion out of the excited region, which could be neglected if the diffusion

Figure 4.11: (a) Fluence dependence (at room temperature) and (b) temperature (at fluence $1.3 \mu\text{J}/\text{cm}^2$) dependence of relaxation time τ_{A1} obtained from low fluence experiments. The solid red lines represent for the energy relaxation time τ_E from TTM.

process is relatively slow.

The expression of energy transfer rate $H(T_e, T_l)$ is [29]:

$$H(T_e, T_l) = f(T_e) - f(T_l), \quad (4.4)$$

$$f(T) = 4g_\infty \frac{T^5}{\theta_D^4} \int_0^{\theta_D/T} \frac{x^4}{e^x - 1} dx. \quad (4.5)$$

Here θ_D is Debye temperature, and g_∞ is electron-phonon coupling constant. The relaxation rate of the energy transfer process could be described by energy relaxation

time τ_E [29]:

$$\tau_E = \frac{\gamma [T_e^2(0) - T_l^2(0)]}{2H(T_e, T_l)}, \quad (4.6)$$

where the temperature of electron system at the moment after photoexcitation $[T_e(0)]$ can be estimated by [29]

$$T_e(0) = \sqrt{T_l(0) + \frac{2U_l}{\gamma}}. \quad (4.7)$$

Here U_l is energy density of pump pulse, and γ is electronic specific heat coefficient. To analyze our results with TTM, γ and θ_D of BSTS have been calculated from heat capacity, which is measured by Physical Properties Measurement System (PPMS) by Quantum Design. The specific heat data of BSTS is shown in Fig. 4.12, and it could be fitted to Debye model and yields $\theta_D = 156$ K. While the value of γ could be obtained from fitting of low temperature data to $C_p = \gamma_p T + \alpha T^3 + \beta T^5$ [31], which yields $\gamma = 1.3 \pm 0.7$ mJ·mol⁻¹K⁻² [(4.7 ± 2.7) J·m⁻³K⁻²]. Such value is consistent with the value in Sb₂Te₃ [(0.7 ± 0.7) mJ·mol⁻¹K⁻²] [31] and Bi₂Se₃ [~2 mJ·mol⁻¹K⁻²] [28]

Fitting results of TTM τ_{A1} as a function of pump fluence and temperature could be fitted well to energy relaxation time τ_E from TTM (Eq. 4.4-Eq. 4.7, fitting curves are shown in Fig. 4.11). From the fittings, the value of electronic specific heat coefficient and electron-phonon coupling constant could be obtained. The fitting from $\tau_{A1}(T, \text{Fluence} = 1.3 \mu\text{J}/\text{cm}^2)$ yields $\gamma = 3.9$ J·m⁻³K⁻² and $g_\infty = 1.1 \times 10^{15}$ W·m⁻³K⁻¹, while the fitting from $\tau_{A1}(T = 300 \text{ K}, \text{Fluence})$ yields $\gamma = 6.4$ J·m⁻³K⁻² and $g_\infty = 1.7 \times 10^{15}$ W·m⁻³K⁻¹. The values of γ are consistent with that extracted from heat capacity measurement [$\gamma_p = (4.7 \pm 2.7)$ J·m⁻³K⁻²].

In metals, the electron-phonon relaxation time could be obtained from the theory of thermal relaxation of electrons [32]:

$$\frac{1}{\tau_E} = \frac{3\hbar\lambda \langle \omega^2 \rangle}{\pi k_B T_e}, \quad (4.8)$$

Figure 4.12: Specific heat of BSTS measured from PPMS. Low temperature data is shown in the inset. Solid lines represent the fitting curve to Debye model of specific heat.

where λ is the dimensionless electron-phonon coupling constant and $\langle\omega^2\rangle$ is the second moment of the phonon spectrum. From the relaxation time at 300 K, $\tau_{A1} = (1.4 \pm 0.2)$ ps, we obtain $\lambda \langle\omega^2\rangle = (4.2 \pm 0.6) \times 10^{25} \text{ Hz}^2 = (18.3 \pm 2.6) \text{ meV}^2$. By use of $\langle\omega^2\rangle = 1.4 \times 10^4 \text{ K}^2$ obtained from Debye model, we calculate $\lambda = (0.17 \pm 0.03)$. The value of λ in our BSTS sample is similar to that of metals such as chromium (0.13 ± 0.02), gold (0.13 ± 0.02), [33] and is consistent with the reported values for Bi_2Se_3 ($0.08 - 0.43$) [34–36].

Limitation of TTM In low frequency ($\sim 1 \mu\text{J}/\text{cm}^2$) experiments, TTM could describe the carrier dynamics in BSTS by using electron-phonon interaction very well. However, it fails to explain the high fluence ($\sim 1 \text{ mJ}/\text{cm}^2$) results: (1) Although τ_{A1} from high-fluence experiments is ~ 1 ps, which is similar to the one from low fluence experiments, it shows different fluence dependence — decreasing with increasing fluence. Such behavior is opposite to TTM. (2) The rise time of $\Delta R/R$ in high-fluence experiments is ~ 700 fs, which is much longer than the one from low

fluence experiments and other metals. (3) The value of γ obtained from TTM fitting with the data of high fluence experiments is much larger than the one of low-fluence experiments.

There are several reasons that might induce the failure of TTM in high fluence experiments, such as large population of optical phonon and considerable electron-hole pairs generation. According to our previous analysis of the number of photons in each pump pulse, in high fluence experiments, most of photons will be used to excite electrons in the bulk for interband transition, and generate a large number of photoinduced electron-hole pairs. Obviously, TTM can not describe the interaction of electron-hole interaction. Moreover, the longer rise time we observed in the high-fluence experiment suggests that in such condition, the underlying crystal structure might be changed (an example is the atomic displacement induced by pump beam, which leads to bandgap change in Bi_2Te_3 [37]) by the population of a large number of electronic excitations, which influences both the lattice dynamics and the strength of electron-phonon coupling transiently. It is obvious that the stronger the electron-phonon coupling can induce more electronic energy is transferred, and effectively slows down the energy accumulation of electronic degrees of freedom, giving rise to a longer rise time in the pump probe signal. Moreover, longer rise time in the pump probe signal might be the result of a slower buildup of photoexcited carriers, which is caused by the emission and reabsorption of optical phonons. Such long rise times have been seen in pump-probe data of bilayer graphene intercalated with sulfate-covered gold nanoparticles [38] as well as in FeCl_3 , [39].

4.3.3 Phonon dynamics

Because of much higher SNR, the data from high fluence ($\sim 1 \text{ mJ/cm}^2$) experiment could reveal the dynamics of phonons more clearly. Therefore, the studies of oscillatory signals is based on the data from high fluence experiments. There are two oscillatory components in $\Delta R/R$, which arise from coherent phonons.

Figure 4.13: (a) The dephasing time τ_{B1} and (b) frequency f_{B1} of the coherent optical phonon. Solid curves are the fits to anharmonic model described by Eqs. (4.9). (c) The dephasing time τ_{B2} and (d) frequency f_{B2} of the coherent acoustic phonon.

Coherent optical phonon According to the discussion in Chapter 2, generation mechanism of coherent optical phonon in pump-probe measurements on BSTS should be displacive excitation of coherent phonons (DECP) [23]. In DECP, after the pump excitation, the quasiequilibrium coordinates of nuclear are displaced without changing the symmetry of lattice, leading to a coherent vibration of the phonon mode about the displaced quasiequilibrium [40]. As shown in Fig. 4.13, the frequency of damped oscillation signal with shorter period is ~ 1.9 THz. Such frequency should come from A_{1g} symmetric optical coherent phonon, which is quite common in similar topological insulators [15, 17, 18, 27, 41]. It is obvious that dephasing time τ_{B1} and frequency f_{B1} are temperature-dependent. With temperature increasing, both τ_{B1} and f_{B1} decrease, which suggests phonon softening. Such phonon softening could be explained by anharmonic effect in vibrational potential energy, i.e. interaction between phonons [42, 43]. Considering the phonon self-energy with three-phonon corrections, the temperature dependent frequency and dephasing time could be

expressed as [42, 43]:

$$\begin{aligned}\frac{1}{\tau_{B1}} &= \gamma_0 + C_1 \left[1 + \frac{2}{\exp\left(\frac{hf_0}{2k_B T} - 1\right)} \right], \\ f_{B1} &= f_0 + C_2 \left[1 + \frac{2}{\exp\left(\frac{hf_0}{2k_B T} - 1\right)} \right].\end{aligned}\tag{4.9}$$

Here γ_0 (disorder-induced damping), f_0 (phonon frequency without considering anharmonic effect), C_1 and C_2 are fitting parameters. With the fitting of τ_{B1} and f_{B1} to Eq. 4.9, we can obtain $f_0 = 1.992 \pm 0.002$ THz and $\gamma_0 = 0.16 \pm 0.01$ THz, which are similar to the values for Bi_2Te_3 ($f_0 = 1.908$ THz and $\gamma_0 = 0.04$ THz) [43].

Coherent acoustic phonon The parameters (τ_{B2} and f_{B2}) of low frequency damped oscillatory signal does not show very obvious temperature dependence. Similar to many OPOP studies of semiconductors and metals, in BSTS, coherent acoustic phonon (CAP) is the origin of low frequency oscillations, which could be explained with the strain pulse propagation model [44].

In OPOP experiment, at the surface of sample, a layer of strain with different dielectric function from unexcited volume could be generated by pump pulse and then propagate in the crystal, which can modulate $\Delta R/R$. In this strain pulse propagation model [44], the frequency of CAP could be expressed as:

$$f_{B2} = \frac{2nv_s \cos(\theta)}{\lambda_{probe}},\tag{4.10}$$

where n is the refractive index of BSTS, v_s is sound speed in BSTS, θ is the incident angle ($\sim \pi/12$), and λ_{probe} is the wavelength of probe beam. The average sound speed of BSTS in 10-300 K range could be estimated as $v_s = 3.22 \times 10^3$ m/s by assuming $n = 5.4$, which is the refractive index of Bi_2Se_3 [20]. The value of v_s is consistent with the one in similar material – Bi_2Te_3 ($v_s = 3.22 \times 10^3$ m/s,¹). Then

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¹Calculated from $v_{11} = \sqrt{C_{11}/\rho}$ where the elastic constant $C_{11} = 6.85 \times 10^{11}$ dyn/cm² and density $\rho = 7.86$ g/cm³. Parameters from J. O. Jenkins, J. A. Rayne, and R. W. Ure, Phys. Rev. B **5**, 3171 (1972)

according to the relation between penetration depth ζ and dephasing time τ :

$$\zeta = v_s \tau, \quad (4.11)$$

we can obtain the $\zeta = 27$ nm of probe beam in BSTS, which is similar to the value in Bi_2Se_3 [20].

4.4 Conclusion

In conclusion, we studied the photoinduced change in reflectivity of the BSTS topological insulator to reveal the dynamics of carriers and coherent optical/acoustic phonons, with the information of Debye temperature and electronic specific heat coefficient obtained from thermodynamic measurements.

Two-temperature model was applied to explain the fast relaxation process of carriers in the conduction band. The obtained dimensionless electron-phonon coupling constant (λ) is consistent with those of conventional metals and Bi_2Se_3 topological insulator. Meanwhile, the validity of two-temperature model in BSTS makes it a good tool to study similar materials [45].

In the study of coherent phonons, anharmonic effects of the A_{1g} coherent optical phonon was used to explain the temperature dependence of the frequency and dephasing time of the high-frequency oscillatory signal. Finally, applying the strain pulse propagation model to the coherent acoustic phonon yields a penetration depth of 27 nm in BSTS for 800 nm laser light.

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Chapter 5

Terahertz Conductivity of Ta-doped TiO_2 : Interacting Polaron Gas Model

In this chapter, the properties of Ta-doped TiO_2 was investigated by using THz-TDS. The interacting polaron gas theory was applied to describe the temperature dependence of the carrier scattering rate, which shows a decrease of the electron-phonon interaction with increasing carrier density.

5.1 Introduction

Because of its diverse applications, TiO_2 has become one of the most important semiconductors. It could be utilized in chemical catalysis [1,2], solar cells [3] and some electronic devices [4] due to its special electronic structure. Intrinsic TiO_2 only absorbs ultraviolet light because of its large bandgap. As a semiconductor, doping can change the properties of TiO_2 in various ways. Anionic doping in TiO_2 could narrow its bandgap [5–8], making the absorption spectrum wider. However, the effects of cationic dopants are more interesting [9–13]. In recent decades, some researches focused on the ferromagnetic doping in TiO_2 because of its potential

application in diluted magnetic semiconductor [14–17]. The abundant properties of TiO_2 with different doping makes it become a very intensely-researched material for both applications and fundamental researches.

There are three major crystal structures (phases) of TiO_2 in nature — rutile, anatase and brookite. The brookite phase has not been studied much due to a lack of applications compared to the other two phases. Both rutile and anatase belong to tetragonal structure, but rutile belongs to space group $P4_2/mnm$ [18] [Fig. 5.1 (a)] with lattice parameters $a = b = 4.587 \text{ \AA}$, $c = 2.954 \text{ \AA}$ [19], while anatase belongs to $I4_1/amd$, [Fig. 5.1 (b)] with lattice parameters $a = b = 3.782 \text{ \AA}$, $c = 9.502 \text{ \AA}$ [19].

Figure 5.1: Crystal structure of rutile and anatase TiO_2 . Red and grey balls represent for oxygen and titanium atoms respectively.

The band structure of anatase (a phase of TiO_2 with tetragonal symmetry) TiO_2 calculated from various DFT methods is shown in Fig. 5.2. The bandgap of anatase TiO_2 is $\sim 3.2 \text{ eV}$ ($\sim 390 \text{ nm}$), which is in the UV range. Also, its band structure shows that anatase TiO_2 is an indirect band gap semiconductor. The large bandgap of TiO_2 makes it transparent in the visible light regime. Therefore, if some shallow defect states can be introduced in the crystal, TiO_2 can become a transparent conducting oxide (TCO).

Figure 5.2: Band structure of anatase TiO_2 calculated from different methods: gray lines = standard DFT calculations, black line = DFT + U calculations and the blue discs = GW calculations using DFT + U. Standard DFT is unable to get accurate band structure of TiO_2 because of the failure of local density approximation in this system. (Taken from Ref. [20])

5.1.1 Applications of TiO_2

The interesting properties of intrinsic and doped TiO_2 makes it suitable for many applications, such as photocatalyst [1, 2], corrosion protective coating [21], gas sensors [22, 23], in solar cells [3], in electronic devices [4] and so on.

Since the discovery of TiO_2 photocatalyst to water splitting at 1972 [24], much attention has been focused on the photo-catalysis performance of TiO_2 . Its mechanism has been explained and well understood by band theory of semiconductors and electrochemistry [25]. In water splitting, electrons and holes are generated in the TiO_2 electrode (anode), then the photo-induced electrons in TiO_2 move to the Pt cathode where they induce reduction reactions, while the photo-induced holes remain in the anode and migrate to its surface where they induce oxidation reactions. Therefore,

the charge separation of electrons and holes is without doubt the most important process in photocatalysis employing semiconducting materials [25]. Similar to water splitting, the application of TiO_2 in dye-sensitized solar cells (DSSCs) [26] is based on the charge separation as well (see in Fig. 5.3) — photo-induced electrons and cation (dye^+) are generated from neutral dye, the electrons move through TiO_2 and external circuit, which constitutes the current, while the cation could be reduced by the redox pair in electrolyte, finally the balance of redox pair in electrolyte could be compensated by the electrons from external circuit. Carriers play important roles in these processes. Therefore, to optimize the photocatalysis of TiO_2 and further improve the performance of DSSCs, the study and understanding of the carriers' behavior in TiO_2 is critical and necessary.

Similar to the application mentioned above, doped TiO_2 as a transparent conducting oxides received much attention because of the development of information technology and the need for new TCOs. TCOs are materials which are both conductive and transparent in visible light regime. It is very useful in many fields, especially in photonics and information technology. Up to present, the most widely used TCO is indium tin oxide (ITO) [28], but as a rare metal, the exhaustible indium reserves on the earth limits its application in the future. Furthermore, in some applications, there are diverse needs [29] for TCOs (i.e. suitable work function and refractive index), where ITO is not enough. Therefore, it is necessary to search for some new TCOs beyond ITO. Recently, Ta/Nb doped TiO_2 has been found to be good TCOs [29], which has similar carrier density and mobility [30] as ITO. As conducting materials, it is necessary to study the nature of carriers in Ta/Nb doped TiO_2 , which will be helpful in their subsequent applications.

5.1.2 Ta-doped TiO_2

The conductivity of Ta-doped TiO_2 is highly dependent on the doping concentration. To obtain ideal conductivity, the concentration of Ta dopant should be about 5 at.% [30]. The carrier density n and mobility μ of Ta-doped TiO_2 with such

Figure 5.3: The basic principle (a) and (b) related energy levels of DSSC. HTM = hole-transport materia. (Taken from Ref. [27])

doping concentration is $\sim 10^{21} \text{ cm}^{-3}$ and $\sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively [31], which is comparable to ITO. Meanwhile, the transmittance of such sample is quite high in visible range, which is acceptable for most applications as a TCO (Fig. 5.4). Some research shows that the optical spectrum [32] as well as the bandgap of Ta-doped TiO_2 is highly dependent on the doping concentration, which is related to its carriers' behavior.

It has been predicted theoretically [33] that Ta doping could (1) introduce an energy level in the gap, and (2) enlarge its bandgap. The mid-gap level comes from

Figure 5.4: (a) UV-vis transmission spectra of pure and Ta-doped TiO₂ samples. (b) Blue shift of the optical bandgaps of anatase Ta-doped TiO₂. Taken from Ref. [32]

a Ti-centered small polaron, which corresponds to self-trapped electron. Optical experiments have confirmed these two effects [31].

5.1.3 Polaron

Polaron is a quasiparticle that usually occurs in polar semiconductor, which contains a conduction electron/hole together with its self-induced polarization (Fig. 5.5) [34]. Depending on the coupling strength (Fröhlich coupling constant α – the larger α , the stronger electron-phonon coupling), polaron could be classified as small polaron ($\alpha > 3$) and large polaron ($\alpha < 3$). Usually, small polarons cannot contribute to a sample's conductivity because of its strong electron-phonon coupling, which “traps” the carrier. However, large polarons, which can move freely in crystal, could be treated as free carriers in materials.

Due to the polar nature of TiO₂, the carriers in Ta-doped TiO₂ should be polarons rather than bare electrons. On the other hand, the high conductivity makes the small polaron in Ta-doped TiO₂ [31,33] unlikely be the main carriers. Therefore, the large polaron should be the mechanism of conduction in Ta-doped TiO₂. ARPES study [36] has confirmed the large polaronic nature of electrons in TiO₂, and gave the value of $\alpha \approx 2.5$. However, according to previous experiments [30], at optimum Ta doping (~ 5 at.%), the carrier density is $\sim 10^{21} \text{ cm}^{-3}$, which is quite large,

Figure 5.5: Schematic of polaron. Taken from Ref. [35].

so the simple polaron model might fail to explain the carriers' behavior. The large carrier density results in small inter-polaron distance, so polaron-polaron interaction therefore cannot be ignored. Therefore, in order to understand this material (optical and electrical properties) more accurately, it is necessary to search for new theory and/or method to study the motion of carriers in such materials. Fortunately, the theory of interacting polaron gas model has been supposed which might be suitable to describe high density polarons [37]. On the other hand, THz-TDS is able to obtain the frequency-dependent conductivity of materials, which could provide more information than traditional DC transport measurement. The combination of interacting polaron gas model (theory), and THz-TDS measurement (experiment), can give us a deeper understanding of the nature of carriers in Ta-doped TiO_2 .

5.2 Experimental information

Three Ta-doped TiO_2 thin films (Fig. 5.6) were grown on SrLaAlO_4 (SLAO) substrate by pulsed laser deposition (PLD) method. During the sample preparation, the temperature was controlled at 880 K, while the oxygen partial pressures were 1×10^{-4} Torr, 1×10^{-5} Torr and 5×10^{-5} Torr for sample A, B and C respectively. These samples were grown by Prof. T. Venky Venkatesan's group from the National

Figure 5.6: Three samples with different growth conditions on SLAO substrates. (The dirty is residue of glue after RBS measurements, which is at the back side of substrate)

The thickness of sample A, B and C were measured as 158.1 nm, 145.2 nm and 210.7 nm by Rutherford backscattering (RBS) respectively, which will be used for THz-TDS data analysis later. The DC conductivity of these three samples were taken by Hall conductivity measurements as well, which agrees with previous research [31]. From the DC conductivity we obtained, carrier densities of three samples are found to be temperature independent, to be $0.5 \times 10^{21} \text{ cm}^{-3}$, $1.3 \times 10^{21} \text{ cm}^{-3}$ and $1.5 \times 10^{21} \text{ cm}^{-3}$ for sample A, B and C respectively, which agree with previous research [31].

The THz transmittance of three samples were taken by TPS-3000 spectrometer as mentioned in Chapter. 2. In our experiments, the temperature was controlled from 10–300 K with vacuum $\sim 10^{-6}$ mbar in cryostat. The sample holder was chosen 3.5 mm diameter to fit the sample size. The result of vacuum-to-vacuum measurement (measure the transmittance without mounting sample and reference), indicates the stability and available frequency range of the system as shown in Fig. 5.7. The transmittance is 100% with fluctuation less than 1% in the range 0.3–2.7 THz, which shows excellent status of the setup. Moreover, in the THz optical path, humidity is suppressed to $\sim 1\%$ by dry air to avoid the absorption of THz

radiation by water vapor.

Figure 5.7: Vacuum to vacuum signal for testing THz-TDS system. [Transmittance of sample (= vacuum) and reference (= vacuum)]

5.3 Results and discussions

5.3.1 THz-TDS data

THz-TDS data of sample A, B, C and reference were taken with time step 0.002 ps in the range -5–15 ps. Fig 5.8(a) shows the transmitted electric field of sample A at selected temperatures, the signals of other samples are similar.

With the data analysis method introduced in Chapter 3, transmittance signal of samples in frequency domain could be obtained. Fig 5.8(b) shows the transmittance of sample A, which is obviously temperature-dependent at high temperature ($T > 100$ K), while it changes little at low temperature. The lower transmittance indicates higher absorption and stronger THz response at low temperature. Meanwhile, the relatively flat transmittance in frequency domain without obvious peaks suggests

Figure 5.8: (a) THz-TDS data of sample A at selected temperatures. (b) transmittance data at selected temperatures. (Signal of other samples are similar.)

Drude-like behavior [see Chapter 3].

According to the Eq. 3.3 and related numerical method, conductivities of samples at all temperatures could be obtained. Fig. 5.9 shows the complex optical conductivities [$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$] of three samples at 10 K. Both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of each sample in frequency domain shows Drude-like shape with different absolute values.

Before analyzing conductivities we obtained, several properties of the samples should be clarified: (1) according to the introduction of TiO_2 earlier, the carriers in Ta-doped TiO_2 samples are polarons [36]; (2) because of the very high carrier density ($\sim 10^{21} \text{ cm}^{-3}$), the average electron-electron distance is $<1 \text{ nm}$, which is of the order of the polaron radius ($\sim 1 \text{ nm}$, see Ref. [36]) and lattice constant of anatase TiO_2 ($a = 0.38 \text{ nm}$, $c = 0.95 \text{ nm}$). Therefore, the interaction between carriers (polarons) should not be neglected. Considering both electron-phonon and electron-electron interactions, as well as the Fermi statistics of the polaron gas,

Figure 5.9: Real and imaginary conductivity of samples, the curves comes from interacting many-body gas theory fitting. (a) sample A, (b) sample B and (c) sample C

interacting polaron gas model [37] should be applied.

5.3.2 Interacting many-polaron gas theory

The start point of the theory is Fröhlich Hamiltonian, which describes the interacting many-polaron gas [37]:

$$\begin{aligned}
 H = & \sum_{\mathbf{k}} \sum_{\sigma=\pm 1/2} \frac{\hbar^2 k^2}{2m_b} c_{\mathbf{k},\sigma}^\dagger c_{\mathbf{k},\sigma} + \sum_{\mathbf{q}} \sum_{j=1}^n \hbar \omega_{L,j} a_{\mathbf{q},j}^\dagger a_{\mathbf{q},j} \\
 & + U_{e-e} + \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \sum_{j=1}^n \left(V_{\mathbf{q},j} a_{\mathbf{q},j} \sum_{\mathbf{k}} \sum_{\sigma=\pm 1/2} c_{\mathbf{k},\sigma}^\dagger c_{\mathbf{k},\sigma} + \text{H.c.} \right).
 \end{aligned} \tag{5.1}$$

$$V_{\mathbf{q},j} = \frac{\hbar \omega_{L,j}}{q} \left(\frac{4\pi \alpha_j}{V} \right)^{1/2} \left(\frac{\hbar}{2m_b \omega_{L,j}} \right)^{1/4} \tag{5.2}$$

$$U_{e-e} = \frac{1}{2} \sum_{\mathbf{q} \neq 0} \frac{4\pi e^2}{\epsilon_\infty q^2} \sum_{\mathbf{k}, \mathbf{k}', \sigma, \sigma'} c_{\mathbf{k}+\mathbf{q},\sigma}^\dagger c_{\mathbf{k}'-\mathbf{q},\sigma'}^\dagger c_{\mathbf{k}',\sigma'} c_{\mathbf{k},\sigma} \tag{5.3}$$

Here $c_{\mathbf{k},\sigma}^\dagger$ and $c_{\mathbf{k},\sigma}$ are the creation and annihilation operators for an electron with momentum $\mathbf{k}$ and spin z-projection σ respectively. $a_{\mathbf{q},j}^\dagger$ and $a_{\mathbf{q},j}$ are the creation and annihilation operators for a phonon with momentum $\mathbf{q}$ and phonon frequency ω respectively. α is the Fröhlich coupling constant.

With random-phase approximation, the consideration of Fermi statistics and the electron-electron interaction, the conductivity of interacting many-body polaron gas could be expressed as [37]:

$$\tilde{\sigma}(\omega) = \frac{e^2 n}{m_b} \frac{1}{i\chi(\omega)/\omega - i\omega}, \quad (5.4)$$

where $n = N/V$ is carrier density, m_b is band effective mass. $\chi(\omega)$ is the memory function, which contains all the information of polaron gas [37]:

$$\begin{aligned} \chi(\omega) = & \sum_j \frac{\alpha_j \hbar \omega_{L,j}^2}{6\pi^2 N m_b} \left(\frac{\hbar}{2m_b \omega_{L,j}} \right)^{\frac{1}{2}} \int d\mathbf{q} \left\{ g(\mathbf{q}, \omega - \omega_{L,j}) \right. \\ & + g^*(\mathbf{q}, -\omega - \omega_{L,j}) - g(\mathbf{q}, -\omega_{L,j}) - g^*(\mathbf{q}, -\omega_{L,j}) \\ & + \frac{1}{e^{\beta \hbar \omega_{\mathbf{q},j}} - 1} \{ G^R(\mathbf{q}, \omega - \omega_{L,j}) + [G^R(\mathbf{q}, -\omega - \omega_{L,j})]^* \\ & \left. - G^R(\mathbf{q}, -\omega_{L,j}) - [G^R(\mathbf{q}, -\omega_{L,j})]^* \} \right\}, \end{aligned} \quad (5.5)$$

where $\omega_{L,j}$ and α_j are the frequency and electron-phonon coupling constant of the j -th LO phonon that is engaged in the polaron respectively. Also, G^R is Green's function:

$$G^R(\mathbf{q}, \omega) = \frac{\hbar V P^{(1)}(\mathbf{q}, \omega)}{1 - \frac{4\pi e^2}{\epsilon_\infty q^2} P^{(1)}(\mathbf{q}, \omega)}, \quad (5.6)$$

where ϵ_∞ is high frequency dielectric constant. $P^{(1)}(\mathbf{q}, \omega)$ is polarization function of the free electron gas:

$$P^{(1)}(\mathbf{q}, \omega) = \frac{1}{V} \sum_{\mathbf{k}, \sigma} \frac{f_{\mathbf{k}+\mathbf{q}, \sigma} - f_{\mathbf{k}, \sigma}}{\hbar \omega + \frac{\hbar^2 (\mathbf{k}+\mathbf{q})^2}{2m_b} - \frac{\hbar^2 \mathbf{k}^2}{2m_b} + i\delta}. \quad (5.7)$$

The imaginary part of function $g(\mathbf{q}, \omega)$ could be obtained from the relationship:

$$(1 - e^{-\beta\hbar\omega}) \text{Im} [g(\mathbf{q}, \omega)] = \text{Im} [G^R(\mathbf{q}, \omega)]. \quad (5.8)$$

and its real part $\text{Re} [g(\mathbf{q}, \omega)]$ could be calculated according to Kramers-Kronig relation.

It is necessary to mention that the imaginary part of polarization could be calculated analytically, which greatly shortens the calculation time. According to our derivation, the expression of $\text{Im}P^{(1)}(q, \omega)$ is:

$$\text{Im}P^{(1)}(q, \omega) = \frac{m^2}{2\pi\hbar^4\beta q} \ln \left| \frac{1 + e^{\frac{\hbar^2\beta}{2m}(\frac{m\omega}{\hbar q} + \frac{q}{2}) + \beta E_f}}{1 + e^{\frac{\hbar^2\beta}{2m}(\frac{m\omega}{\hbar q} - \frac{q}{2}) + \beta E_f}} \right|. \quad (5.9)$$

The analytical expression of $\text{Im}P^{(1)}$ agrees with that in Ref. [38], which confirms the validity of our derivation.

Calculation of $\chi(\omega)$ According to the Eq. 5.5 – Eq. 5.8, $\chi(\omega)$ of our samples could be simulated. The simulation parameters are in Table 5.1.

Table 5.1: Simulation parameters of $\chi(\omega)$

Sample	n ($\times 10^{21} \text{ cm}^{-3}$)	m_b/m_0 Ref. [39]	$E_f(\text{eV})$ Ref. [32]	ϵ_∞ Ref. [40]	$\omega_L/2\pi$ (THz) Ref. [41]
A	0.5	0.83	0.22	16	11.0, 26.3
B	1.2	0.87	0.28	16	11.0, 26.3
C	1.3	0.87	0.28	16	11.0, 26.3
D	1.5	0.87	0.29	16	11.0, 26.3

Here the value of carrier density was obtained from Hall effect measurements as shown in the section of experimental information. Band effective mass m_b was calculated from Eq. 5.10 and data from Ref. [39]. ϵ_∞ was calculated from reflectivity $R(\omega)$ (see Eq. 5.11) and data from Ref. [40].

$$\frac{1}{m_b} = \frac{1}{m_x} + \frac{1}{m_y} + \frac{1}{m_z}, \quad (5.10)$$

$$R(\omega) = \left| \frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1} \right|^2. \quad (5.11)$$

During the calculation, α_j is assumed to be 1, and will be fitting parameters in the subsequent data analysis. The simulation results are shown in Fig. 5.10. It is obvious that the temperature dependence of $\text{Im}[\chi(\omega)]$ is more significant than $\text{Re}[\chi(\omega)]$, especially in low-frequency regime. Moreover, by checking the low-frequency limit of the results, we can find that in the low-frequency regime ($\omega < \omega_{LO}$), $\text{Im}[\chi(\omega)]$ is proportional to ω while $\text{Re}[\chi(\omega)]$ is proportional to ω^2 , which is consistent with Ref. [42]. The frequency and temperature dependence of $\chi(\omega)$ are similar for the three samples, with the difference being that, for low-doping concentration sample, the absolute value of $\text{Re}[\chi(\omega)]$ and $\text{Im}[\chi(\omega)]$ is larger.

5.3.3 Analysis of conductivity

Considering the contribution from carrier scattering of defect (γ_{defect}), which is temperature-independent [43], the model for the conductivity of our samples could be modified as

$$\tilde{\sigma}(\omega) = \frac{e^2 n}{m^*} \frac{1}{\gamma_{\text{total}} - i\omega}, \quad (5.12)$$

where the total scattering rate γ_{total} is defined as

$$\gamma_{\text{total}}(\omega) = \gamma_{\text{defect}} + i \frac{\chi(\omega)}{\omega}. \quad (5.13)$$

Here we replaced the band effective mass (m_b) with polaron effective mass (m^*) by considering the sum rule for polaron (Eq. 5.14) [42], which shows that in low-frequency range ($\omega < \omega_{LO}$), the conductivity spectral weight was contributed from the polaron effective mass rather than band effective mass. Then we can fit the conductivity data to Eq. 5.12 to obtain γ_{total} and m^* as functions of temperature (Fig. 5.11) for the three samples [37, 42].

Figure 5.10: $\chi(\omega)$ of sample A (a), B (b) and C (c). The dot and solid curves represent for $\text{Re}[\chi(\omega)]$ and $\text{Im}[\chi(\omega)]$ respectively.

$$\frac{\pi e^2 n}{2m^*} + \int_{\omega_{LO}}^{\infty} \text{Re} [\tilde{\sigma}(\omega)] d\omega = \frac{\pi e^2 n}{2m_b}. \quad (5.14)$$

The IR spectrum of pure anatase TiO₂ [41], suggests that only two LO phonon modes of frequency 366 cm⁻¹ (10.97 THz) and 876 cm⁻¹ (26.26 THz) should be considered in the calculation of $\chi(\omega)$. Furthermore, the effective Fröhlich coupling constant $\alpha_{\text{eff}} = \sum_j \alpha_j$, defined in Ref. [37] is also calculated.

Table 5.2: Phonon frequency, Fröhlich coupling constant of different samples

Sample	Nominal doping (at.%)	Carrier density ($\times 10^{21}$ cm ⁻³)	α_{eff} = $\alpha_1 + \alpha_2$	α_1 10.91 THz	α_2 26.26 THz
Pure anatase TiO ₂	-	$\sim 10^{-2}$	~ 2.5	-	~ 2.5
A	2.4	0.5	2.50 ± 0.15	1.36 ± 0.05	1.14 ± 0.10
B	6.9	1.3	2.09 ± 0.10	2.09 ± 0.10	—
C	6.2	1.5	1.05 ± 0.08	1.05 ± 0.08	—

Table 5.2 gives the values of α_j corresponding to phonon mode j . Our results show that the 26-THz phonon mode is not involved with polaron formation in Samples B and C, whose doping concentrations are higher than that of Sample A. However, ARPES measurements in pure anatase TiO₂ revealed quasiparticle bands whose energy difference suggests a phonon energy of 108 meV (26.3 THz) [36], indicating that polaron formation originates mainly from the coupling between electron and 26.3-THz phonon mode, not the 11-THz phonon mode. This suggests that, with increasing Ta doping, there is greater contribution from the low-frequency (11-THz) phonon mode, and correspondingly smaller contribution from the high-frequency (26-THz) phonon mode, in polaron formation. Recent Raman data suggest that the presence of Ta dopants have modified the phonon spectrum (change in both intensities and positions of phonon peaks) [44], which could then change the coupling between the electron and the phonon modes.

Moreover, Table 5.2 shows that the values of α for all the samples are smaller than 3, which is consistent with the large-polaron scenario. Furthermore, we see that the higher the carrier density, the smaller the electron-phonon coupling (α_{eff}) — this can be explained by stronger screening arising from the higher electron density

Figure 5.11: Fitting results of Eq. 5.12: (a) real part of γ_{total} , (b) imaginary part of γ_{total} and (c) effective mass of three samples. The curves in (a) represents for the scattering rate calculated from polaron.

and/or change in phonon spectrum. Figure 3 shows that the value of $\text{Im}(\gamma)$ is one order of magnitude smaller than $\text{Re}[\gamma(T = 300 \text{ K})]$ at all temperatures, and does not any temperature dependence, which is consistent with our simulation of $\chi(\omega)$ in Fig. 5.10.

On the other hand, in high Ta-doped samples, the (1) low scattering rate induced by high carrier density and (2) smaller electron-phonon coupling (α), contribute to their higher conductivity.

Finally, we offer two evidences of Ta-doped being an interacting polaronic gas. First, optical (THz to IR) spectroscopy data of Nb-doped SrTiO_3 yielded a large carrier density $n \sim 10^{20} \text{ cm}^{-3}$, which the authors attributed to the presence of an interacting polaronic gas [45]. Our value of carrier density obtained from Hall effect measurements (see the section of Experimental Information above) of $\sim 10^{21} \text{ cm}^{-3}$ is larger than that in Nb-doped SrTiO_3 . This value of carrier density corresponds to a mean inter-polaronic distance of $< 1 \text{ nm}$, which is of the order of the inter-atomic distance. This increases the correlation between adjacent polarons, and makes the notion of an interacting polaronic gas in this material plausible. Second, according to the sum rule in low frequency range [37, 45], from Drude spectral weight W_D , the polaron effective mass m^* could be obtained, which shows in figure 5.11(c). It is obviously that m^* changes significantly between 10 K and 300 K, especially in the samples with high Ta doping. In the conventional large-polaron theory [46], the effective mass $m^* = m_b(1 + \alpha/6)$ is taken to be temperature-independent. Even in the modified Feynman's polaron theory [47], m^* should change by $\sim 10\%$ from 10 K to 300 K. Therefore, the temperature dependence of m^* that we see in our data suggests the presence of many-polaron effects. A similar temperature-dependent effective mass was also observed in Nb-doped SrTiO_3 [45], which the authors attributed to the presence of a polaronic liquid as well.

5.4 Conclusion

In conclusion, THz-TDS measurements on three Ta-doped TiO₂ samples were performed. The conductivity obtained from THz transmission indicates the interacting polaron gas based conductivity mechanism in the materials. Furthermore, the results show that higher carrier density could lead to smaller electron-phonon coupling, which might be from larger screening effect and/or the change of phonon spectrum. The results reveal that the good electronic performance of Ta-doped TiO₂ with higher doping concentration is not only from its high carrier density, but also the less electron-phonon coupling (smaller α).

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Chapter 6

Terahertz Measurements of Amorphous In_2O_3 films

In this chapter, THz-TDS data of amorphous In_2O_3 ($a\text{-In}_2\text{O}_3$) films were presented. The complex optical conductivity obtained were fitted using the Drude model. Our results suggest that, (1) the electronic performance (conductivity, carrier density and mobility) of $a\text{-In}_2\text{O}_3$ is comparable with crystalline In_2O_3 ($c\text{-In}_2\text{O}_3$); (2) the mobility and carrier density of $a\text{-In}_2\text{O}_3$ is highly dependent on the growth temperature; (3) in amorphous phase, the mobility obtained from AC measurement might be different from Hall effect (a DC) measurement.

6.1 Introduction

6.1.1 Amorphous materials

The amorphous phase is a condensed phase without long-range translational order, different from crystals and polycrystals (see in Fig. 6.1). Compared to our daily life, where lots of solid matter surrounding us is in amorphous state (such as glass), studies of amorphous material are comparatively few in the field of condensed matter physics, because of its unknown Hamiltonian induced by random structures, not to mention the solutions of those Hamiltonians. However, some theories of defects

are available to explain some properties of amorphous semiconductors, such as the Anderson localization, which is able to explain the mobility change with Fermi level [1] – if the Fermi level is at localized state, electrons are localized and the conductivity should be small, if electrons are in extended states, the material is with higher conductivity.

Figure 6.1: Comparison between crystal, polycrystal and amorphous material. Taken from Ref. [2].

The short-range order of amorphous materials could be identified by X-ray diffraction (XRD) [3], X-ray absorption spectroscopy (XAS), extended X-ray absorption fine structure (EXAFS) [4], electron diffraction [5] measurement and so on. Those techniques could provide the information about effective coordination number and the average bond-distance, which is helpful to understand the micro structure of amorphous materials. Moreover, transport [4,6] and thermal characterization [7,8] are usually used to study their electric and thermal conductivity as well.

6.1.2 Transparent amorphous semiconductors

Transparent amorphous semiconductors, such as amorphous indium zinc oxide (IZO) and $a\text{-In}_2\text{O}_3$, have attracted more and more attention due to their potentially disruptive technologies. There are several advantages [4] compared with their crystalline counterparts: (1) the growth temperature of amorphous material is low [9], which could simplify the deposition process; (2) because there is no grain boundary in amorphous material, the sample could be more isotropic, uniform and smooth [10–

14]; (3) the random microstructure does not require substrates to be lattice-matched, which makes the choose of substrate easier and extending their applications; (4) the structure of amorphous materials are more liquid-like, hence they are more pliable, leading themselves to the possibility of flexible devices [14]. Moreover, the performance of amorphous materials, such as optical and electric properties, are comparable to their crystalline counterparts [15]. In other words, both the low cost and high quality of amorphous materials make them ideal for optoelectronic applications.

Figure 6.2: Schematic orbital drawing of electron pathway (conduction band) in crystalline (up) and amorphous (down) ionic oxide semiconductors. Taken from Ref. [6]

Most TCOs are ionic materials, in ionic materials, the vacant s-orbitals of a cation, which contribute to conduction band, has a larger spatial extent than 2p-orbitals of oxygen that dominate the valance band. The large extent of the vacant s-orbitals can overlap with other s-orbitals from neighboring cations, and form a conduction channel for electrons [6]. However, for amorphous materials, although similar conduction channels could be formed, the length and angle of the bonds in

the channels could fluctuate randomly, especially for the energetically weak part [6].

Similar to crystalline TCOs (c-TCOs), the properties of amorphous TCOs (a-TCOs) are highly dependent on the growth conditions, due to the sensitivity of bond angles and lengths on growth conditions [16]. Furthermore, the thermal stability of a-TCOs is quite important, because in the application environment, the material usually only retains its desirable properties at a certain temperature range. The amorphous material will change to crystalline counterpart at relatively high temperature [17]. Some related researches [18] suggests that the chemical composition affects the thermal stability of amorphous materials significantly.

6.1.3 Amorphous In_2O_3

Crystalline In_2O_3 is a good TCO [19, 20] with relatively high transparency ($\sim 90\%$ for visible light) and conductivity ($\sim 10^5 \Omega^{-1}\text{m}^{-1}$). It is n-type semiconductor (oxygen vacancies are the donor) with bandgap $> 3.5 \text{ eV}$ [20]. According to previous researches, amorphous In_2O_3 is a good TCO as well, which has performance comparable to c- In_2O_3 [4]. The micro-structure of a- In_2O_3 consists of InO_x ($5 < x < 6$) polyhedra, but the arrangement of such polyhedra is not regular as in crystalline [4]. In Ref. [20], several a- In_2O_3 thin film samples are prepared with different growth conditions, and the results show that: the carrier concentration (see in Fig. 6.3) of a- In_2O_3 is quite high, making it degenerate; In addition, optical measurements on a- In_2O_3 proves that Drude model is adequate to describe its transmittance. Moreover, the absorption edge of a- In_2O_3 shows that its bandgap is larger than 3.3 eV and varies with carrier concentration. Those properties (carrier concentration, transmittance and bandgap) are highly dependent on the growth conditions.

Recently, large-area amorphous In_2O_3 thin films were grown using pulsed laser deposition (PLD) at low deposition temperatures, exhibiting a crystalline phase when grown at 25°C and above, and amorphous phase when grown at 0°C or below. This promises simple and economical large-area growth of this particular a-TCO, and makes possible a wider choice of bendable plastic substrates for the films

Figure 6.3: Resistivity vs. carrier concentration of In₂O₃. Taken from Ref. [20].

to be deposited on. Remarkably, across this crystalline-to-amorphous transition, the carrier mobility exhibits a non-monotonic behavior, peaking at the transition boundary near 0 °C growth temperature (Fig. 6.4). First-principle, transport and X-ray studies suggest that this mobility peak arises from the more inter-connectedness of the InO_x polyhedra that forms a percolating path for the free carriers with such growth condition.

The mobility peak of a-In₂O₃ (Fig. 6.4) could reach to $\sim 60 \text{ cm}^2/\text{Vs}$, which is comparable to the c-In₂O₃ and high quality ITO [21]. Such amazing performance suggests the value of a-In₂O₃ in future applications, and justifies a detailed study of its carrier properties. Another reason for studying amorphous In₂O₃ is that, indium-based TCOs have been widely studied and applied due to their high transmission in visible light range and good conductivity [16,22]. The microstructure of indium-based TCOs is shown in Fig. 6.5. The basic units of such materials are InO₆ and XO_n (X = Zn, Ga, Sn, or Ge) polyhedra, and the electronic properties and conduction mechanism of them are similar. Therefore, the study of a-In₂O₃ is representative

Figure 6.4: Mobility and crystalline fraction of In_2O_3 at different deposition temperature. Taken from Ref. [4].

Figure 6.5: Atomic structures of a-In-X-O , $\text{X} = \text{Zn, Ga, Sn, or Ge}$. Taken from Ref. [22].

and necessary.

However, almost all the previous transport or optical works on indium-based a-TCOs are based on DC transport measurement (~ 0 Hz) or IR spectroscopy (>10 THz), so spectroscopic data in the THz range (0.1–10 THz), which can tell us important properties of carriers and phonons, has not been well studied. In this chapter, THz-TDS conductivity of amorphous In_2O_3 will be measured and modeled.

6.2 Experimental information

Three In_2O_3 thin films were fabricated by PLD [4] at -10 °C, 50 °C and -70 °C (named as sample #1, #2 and #3 respectively). Substrates for the three samples are $10 \times 10 \times 1$ mm z-cut quartz, which are isotropic for normal incident light and transparent for THz radiation. The thickness of #1, #2 and #3 are 260 nm, 250 nm and 230 nm respectively. According to Ref. [4], sample #1 and #3 should be amorphous while sample #2 is a mix of amorphous and crystalline counterparts.

Figure 6.6: a- In_2O_3 films on z-cut quartz substrates. The samples from left to right are grown at -10 °C, 50 °C, -70 °C and pure substrate respectively.

The samples [shown in Fig. 6.6] were mounted on the sample holder for THz-TDS (in Fig. 3.5). The temperature of samples was set from room temperature to 15 K, and back to room temperature with vacuum 10^{-6} mbar to check for possible hysteresis effects.

6.3 Results and discussions

6.3.1 THz-TDS data

THz electric field signal of sample and reference in time domain were obtained as shown in Fig. 6.7(a), which shows a small transmittance ($\sim 10\%$). According to the data analysis method introduced in Chapter 3, transmission of three samples could be obtained from time-domain signal. Transmittance of all the samples [Fig. 6.7(b), (c) and (d)] are relatively flat in frequency domain, suggesting that the response of free carrier, rather than phonon, dominates THz absorption in the samples. Furthermore, there is obvious temperature dependence in transmittance for all the three samples.

Figure 6.7: THz-TDS signal of a-In₂O₃ samples. (a) Electric field in time domain of #1 at 289 K (the remains data are similar); (b), (c) and (d) are the transmittance of THz radiation calculated from THz-TDS data at selected temperatures.

According to the Eq. 3.3 and related numerical method, conductivities of samples at all temperatures could be obtained. Fig. 6.8 shows the complex optical conduc-

tivities $[\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)]$ of three samples at room temperature, the lower temperature data are similar. Both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of each sample in frequency domain shows Drude model behavior. The value of conductivity is $\sim 10^5 \Omega^{-1}\text{m}^{-1}$, which is as good as c-In₂O₃ [4].

Figure 6.8: Conductivities of three a-In₂O₃ thin films at room temperature. (conductivity at lower temperatures are similar). The solid curves represent for Drude model fitting.

6.3.2 Drude model fitting

Since the optical conductivities of three samples are Drude model like, we fitted the data to Drude model introduced in Chapter 3. The deviation between fitting curves and real data are very small as shown in Fig. 6.8, representing very good fitting quality. Fitting parameters — plasma frequency ω_p and scattering rate γ as functions of temperature could be obtained (Fig. 6.9). As mentioned above, the temperature of each measurement was controlled from high to low and then from low to high. There is no obvious hysteresis effect in $\omega_p(T)$ and $\gamma(T)$, which

suggests that the micro-structure of a-In₂O₃ at low temperature are robust for all the samples. The change of ω_p and γ with temperature is very small, representing that the electronic properties of the samples are roughly temperature-independent.

Figure 6.9: (a) Plasma frequency ω_p and (b) scattering rate γ of a-In₂O₃ thin film samples.

According to the expression of plasma frequency Eq. 3.15 and mobility Eq. 3.18,

carrier density n and mobility μ in three samples could be obtained (Fig. 6.10). The effective mass of a-In₂O₃ samples is $0.3m_e$ from Ref. [23]. Similar to ω_p and γ , n and μ does not show obvious hysteresis effect.

Figure 6.10: (a) Carrier density n and (b) mobility μ of a-In₂O₃ thin film samples.

It is obvious that the mobility measured from Hall effect [4] is different from the one we obtained (Table 6.1). A possible explanation is that the conduction mechanism under DC electric field is different from AC (THz) electric field. From

Hall effect measurement, the mobility is taken to be a measure of the mobility which enters into conduction [24]. In DC measurement on a certain sample, the conduction path for carriers should be very long (in principle, the path should link the two probe electrodes). According to the previous research of amorphous In_2O_3 [4], the mobility peak in Fig. 6.4 is attributed to the longer conduction path at $\sim -10^\circ\text{C}$, which confirm the assertion above. While in THz measurements, we can estimate the length of conduction path according to the drift length l_d under THz electric field within 1 THz period ($t_{\text{THz}} \sim 1 \text{ ps}$), $l_d = v_d t_{\text{THz}} = \mu E_{\text{THz}} t_{\text{THz}} \sim 10 \text{ nm}$, here v_d is drift velocity of carriers, E_{THz} is the intensity of THz electric field, which is $\sim 10 \text{ kV/cm}$. Therefore, THz measurement could probe the conduction process with the conduction path longer than 10 nm, which should be different from DC measurements.

Table 6.1: Mobility and carrier density measured by Hall effect (taken from Ref. [25]) measurement and THz-TDS

	#1 (-10°C)	#2 (50°C)	#3 (-70°C)
μ (Hall)	$60 \text{ cm}^2/(\text{V.s})$	$45 \text{ cm}^2/(\text{V.s})$	$20 \text{ cm}^2/(\text{V.s})$
μ (THz)	$120 \text{ cm}^2/(\text{V.s})$	$100 \text{ cm}^2/(\text{V.s})$	$180 \text{ cm}^2/(\text{V.s})$
n (Hall)	$2.0 \times 10^{20} \text{ cm}^{-3}$	$2.6 \times 10^{20} \text{ cm}^{-3}$	$1.8 \times 10^{20} \text{ cm}^{-3}$
n (THz)	$1.4 \times 10^{20} \text{ cm}^{-3}$	$0.9 \times 10^{20} \text{ cm}^{-3}$	$0.7 \times 10^{20} \text{ cm}^{-3}$

Another explanation is the band-bending at the surface of our samples. Band-bending could change the Fermi level, which might shift it to extended states, inducing higher mobility in our samples [1]. To further confirm my explanations, more samples need to be measured in the future.

Similar to other amorphous materials, the carriers in a- In_2O_3 should come from various defects in the microstructure, such as oxygen vacancy or metal interstitial [16]. Therefore, the relation $n(\#1) > n(\#3)$ indicates that sample grown at -10°C has more donors or less acceptors for carriers. Meanwhile, $\mu(\#3) > \mu(\#1)$ is consistent with the smaller scattering rate from fewer defects. Therefore, if we just consider the quantity of defects that related to carrier density, carrier density and mobility is negatively correlated – more carrier indicates less mobility. However, considering some defects without changing carrier density, such as the disorder of

length and angle of bonds, the relationship between carrier density and mobility might be more complex. Therefore, to confirm the relationship between defects and carrier mobility density, more samples need to be measured.

Although the temperature dependence of carrier density (plasma frequency) of all the three samples is not very obvious, we still can see that n decreases slightly with increasing temperature. There are two possible reasons for this temperature dependence: (1) the carrier density is smaller at higher temperature due to the electronic structure change induced by structure variation. (2) the carrier density of a-In₂O₃ does not change with temperature while the effective mass of carrier is larger at higher temperature. Unfortunately, we cannot test the validity of these two hypotheses, because we do not know the temperature dependence of effective mass in this material.

In sample #2, the relatively low carrier density could be explained by the existence of some crystalline region, which contain fewer defects. The smaller mobility should come from the additional scattering from incoherent boundaries between the crystalline and amorphous phases [16]. Therefore, for the purpose of application, the amorphous film with the existence of a large number of crystalline is not a good choice.

6.3.3 Power law fitting

Usually, the conductivity of highly-disordered system with localized carriers could be described by variable-range hopping (VRH) model [26]:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^n \right]. \quad (6.1)$$

However, conductivity of all the three samples obeys the power law:

$$\sigma(T) = \sigma_0 + AT^n. \quad (6.2)$$

The low-frequency conductivity (defined as σ_{DC}) and corresponding power law

Figure 6.11: Low frequency conductivity of three samples vs. temperature. The red curves are the power law fitting.

fitting results of three samples are in Fig. 6.11. The coefficient $A < 0$ and $n \sim 2$ are different from previous research on a-In₂O₃, in which $A > 0$ and $0.33 < n < 1$ [27,28]. The reason for such difference is unknown, so more researches on a-In₂O₃ samples with different growth conditions, should be performed in the future.

6.4 Conclusion

In conclusion, THz-TDS measurements on three amorphous In₂O₃ films were performed. The conductivity obtained from THz transmission could be fitted well by Drude model. The fitting results shows that the electronic performance (conductivity, carrier density and mobility) of a-In₂O₃ is comparable with crystalline In₂O₃ (c-In₂O₃). Furthermore, the sample grown at -10 °C has higher carrier density and lower mobility, which indicates the existence of more defects. Moreover, the sample grown at 50 °C shows worse electronic performance because of the large

number of crystalline in the amorphous phases. Also, according to our results, the measurement of THz (AC) and Hall effect (DC) on amorphous materials might be different.

The THz (AC) mobility is found to be different from the Hall (DC) mobility, which might be the result of band-bending at the surface of our samples or, more interestingly, the result of AC nature of THz radiation and amorphous structure of samples.

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Chapter 7

Conclusions & Future Work

In this chapter, some future works will be proposed. Bilayers of 2D materials and/or topological insulators will be studied by THz-TDS and OPOP. The electron transfers between two dissimilar layers, which would be useful for future applications, will be studied. Meanwhile, fast-scan OPOP system, based on a 250 kHz Ti:sapphire laser, which can accelerate the data taking speed will be built.

7.1 Conclusions of this thesis

To sum up, in this thesis, ultrafast spectroscopy studies of topological insulators were performed, and the properties of carriers in transparent conductive oxides were identified by THz-TDS.

In the OPOP studies of topological insulator BSTS, the transient reflectivity of the sample has been studied, which reveals the dynamics of carriers and coherent optical/acoustic phonons in the material. Meanwhile, the results of thermodynamic measurements yields the Debye temperature and electronic specific heat coefficient of BSTS. We applied a two-temperature model to explain the fast relaxation process of carriers in the conduction band. The obtained dimensionless electron-phonon coupling constant (λ) is consistent with those of conventional metals and Bi_2Se_3 topological insulator. The Anharmonic effects of the A_{1g} coherent optical phonon was used to explain the temperature dependence of the frequency and dephasing

time of the high-frequency oscillatory signal. Finally, applying the strain pulse propagation model to the coherent acoustic phonon yields a penetration depth of 27 nm in BSTS for 800 nm laser light. In this study, OPOP technique proved to be a good tool to study the dynamics of carriers and phonons. Meanwhile, the validity of two-temperature model in BSTS proves that the TTM is a useful model to study similar materials [1]. The obtained electron-phonon constant is a useful parameter to characterize similar thermoelectric materials.

In the THz-TDS study of TiO_2 , the THz conductivities of three samples with different doping concentrations from 10 to 300 K are obtained. Applying the interacting polaron gas theory, the temperature-dependent conductivity could be well explained, which indicates that the carriers in this material are interacting polarons. Furthermore, the results show that more Ta doping could decrease the electron-phonon interaction, which is another origin of the high conductivity of Ta-doped TiO_2 , in addition to the high carrier density. The results indicate that the high conductivity of Ta-doped TiO_2 does not just originate from the high carrier density, but also from its low electron-phonon coupling. In this study, the nature of carriers in Ta-doped TiO_2 was identified as interacting polarons, which is quite different from intrinsic or other doping TiO_2 with low carrier density. This explanation could help us understand the carriers behavior in other doped semiconductors with high carrier density.

Finally, in the THz-TDS study of amorphous In_2O_3 , the terahertz conductivity of three samples with different growth temperature from 10 to 300 K is obtained, which could be fitted well by Drude model. The fitting results shows that the electronic performance (conductivity, carrier density and mobility) of a- In_2O_3 is comparable with crystalline In_2O_3 (c- In_2O_3). Furthermore, the sample grown at -10°C has higher carrier density and lower mobility, which indicates the existence of more defects. Moreover, the sample grown at 50°C shows worse electronic performance because of the mixture of crystalline and amorphous phases. Finally, the power law of low frequency conductivity indicates that there is no localization of carriers

in amorphous In_2O_3 films. In this study, the measured THz (AC) conductivity is found to be different from the Hall (DC) conductivity, which might be the result of band-bending at the surface of our samples or, more interestingly, the result of AC nature of THz radiation and amorphous structure of samples.

7.2 Future work

Based on my current works on topological insulators and some preliminary studies of two-dimensional (2D) materials, my future work will focus on the single layer 2D materials and hetero-bilayers which consist of 2D materials and/or topological insulators. Moreover, to decrease the data taking time of time-resolved THz-TDS measurements, which is time consuming, a fast-scan system was designed and will be built in the future.

7.2.1 Interface of 2D materials and topological insulators

2D materials, which refers to some single-layer materials consisting of one layer of atoms, have become a hot field in condensed matter physics because of their potential applications in photovoltage, electronics and spintronics. Graphene is the first to be found as a 2D material, which is a single layer of carbon atoms with honeycomb structure [2–4]. Its special band structure of linear dispersion near K point, as well as massless carriers, make graphene as a good material for studying new physics [5,6]. Furthermore, the remarkable mechanical, thermal and electronic performance [7,8] of graphene make it a good material for applications.

Except for graphene, more 2D materials [10] such as transition metal dichalcogenides [9] (TMDs: MoS_2 [11], WS_2 [12], WSe_2 [13]), were found. In contrast to graphene, the existence of bandgap makes TMDs are semiconductor like, which have more applications in devices such as field-effect transistors. The properties of TMDs are layer-dependent. For example, bulk MoS_2 is indirect bandgap semiconductor with bandgap 1.3 eV, but the single layer MoS_2 is direct bandgap with bandgap

Figure 7.1: Structure of 2D transition metal dichalcogenides materials. (a) Typical crystal structure of 2D TMDs, X = chalcogen atom (yellow), M = metal atoms (grey). (b) Optical and (c) AFM images of MoS₂. (d) bulk MoS₂. (e) Three structural polytypes of TMDs which contains different symmetries. Taken from Ref. [9]

1.8 eV. More optoelectronic applications could be proposed because of such direct bandgap [14].

Although 2D materials has been widely studied, there are still some questions need to be answered. For example, in the field of traditional semiconductors, the heterojunction is the basis of many applications, such as heterojunction transistors, semiconductor lasers and solar cells [15, 16]. Therefore, similar to that in semiconductors, we must answer the question “what are the electronic properties of heterojunction/hetero-bilayer of 2D materials?”

According to previous DFT studies on hetero-bilayer [17, 18], the band structure of hetero-bilayers of different TMDs are very different from single layer material, as shown in Tab. 7.1. The results indicate that both the value and type of bandgap (direct/indirect) of hetero-bilayer could differ much from single layer very much.

Except for TMDs, graphene and topological insulators could be good components for the hetero-bilayers. Recently, in the research of a composite of Bi₂Te₃ nanopar-

Table 7.1: Bandgap and binding energy of single layer MX_2 (E_{g1}), bilayer MX_2 (E_{g2}) and hetero-bilayer MX_2/MoS_2 (E_{g3}). Taken from Ref. [17]

	E_{g1} (eV)	E_{g2} (eV)	E_{g3} (eV)	E_b (eV)
MoS_2	1.67 Direct	1.25 Indirect	-	-
MoSe_2	1.46 Direct	1.20 Indirect	0.74 Indirect	-0.16
WS_2	1.81 Direct	1.43 Indirect	1.16 Indirect	-0.22
WSe_2	1.55 Direct	1.38 Indirect	0.57 Direct	-0.16
CrS_2	0.93 Direct	0.68 Indirect	0.39 Indirect	-0.14
CrSe_2	0.74 Direct	0.60 Indirect	0.69 Indirect	-0.22
FeS_2	Metal	Metal	Metal	-0.31
VS_2	Metal	Metal	Metal	-0.23
VSe_2	Metal	Metal	Metal	-0.16

ticles deposited on single layer graphene (SLG) [19], the electron injection from TI into graphene was observed, which suggests an interesting interaction between TI and graphene. Therefore, the research on hetero-bilayer of TI and other 2D material is necessary. Furthermore, the preliminary THz-TDS research I performed (see the following paragraph) suggests enhanced conductance of SLG/ WS_2 even at zero bias voltage, which shows some potential in future application.

As mentioned in Chapter 2, THz-TDS could be an excellent technique to study the properties of carriers and phonons in hetero-bilayers in equilibrium state. However, to investigate some non-equilibrium properties, such as photoinduced carriers, we must apply OPTP (see in Chapter 2) technique. Up to present, some OPTP researches on 2D material have been reported. Interesting phenomena, such as trion-induced negative photoconductivity in MoS_2 [20], semiconducting-to-metallic photoconductivity crossover in SLG [21], were found. The carrier dynamics of a few-layer MoS_2 [22] has been investigated by OPTP as well. Therefore, both THz-TDS and OPTP could be good tools to study hetero-bilayers, and will be utilized in my future work.

Preliminary work on hetero-bilayer THz-TDS measurements are performed on single layer WS_2 , SLG and WS_2/SLG hetero-bilayer. The conductance (conductivity $\times$ thickness) of the later two are shown in Fig. 7.2, which are is obviously Drude-Smith like (see in Chapter 3). However, the transmittance of single layer

WS₂ is $\sim 100\%$ for THz radiation, which means there is no terahertz response and free carriers in this material.

Figure 7.2: Complex conductance of WS₂/SLG and SLG films at 15K. The circles and square represent for the experimental data while the lines are fitting curves of Drude-Smith model.

The higher conductivity of WS₂/SLG hetero-bilayer than SLG (see Fig. 7.2) should not come from the contribution of WS₂ directly since there are few free carriers in it. So we suggest that the enhanced conductivity should origin from the interaction between two different layers. Detailed analysis shows that the lower scattering rate (higher mobility) in WS₂/SLG hetero-bilayer is the reason for higher conductivity. However, since the properties of graphene are very sample-dependent, the conductivities of two graphene samples in the same batch can be different. Therefore, more THz-TDS experiments on different samples, or on the sample with different bias voltages are necessary. Moreover, electron ejection from SLG to WS₂ is expected as the found in nanoparticles deposited on single layer graphene (SLG) [19]. In conclusion, the physics in WS₂/SLG hetero-bilayer need to be further investigated

by THz-TDS experiment in the future.

Preliminary work on WSe₂ The valley-dependent properties of TMDs has received a lot of attention, since its potential values in applications [23]. The carriers excited by photon with different polarization can populate different bands, which lead to some spin-related physics. Therefore, the OPTP studies of WSe₂ is performed. The preliminary result is the transient terahertz electric field ($\Delta E/E$) signal, as shown in Fig. 7.3. However, it is obvious that the signal is not polarization dependent. The reason might be the linear polarized terahertz radiation cannot distinguish the carriers with different spins. Therefore, the polarization-sensitive THz-TDS experiments on 2D materials will be performed later.

Figure 7.3: Transient terahertz electric field $\Delta E/E$ of WSe₂ samples from OPTP measurement.

7.2.2 Fast scan OPTP system

Although OPTP technique is very powerful, the data taking of a complete measurement to extract conductivity of sample after pump is time consuming, because

THz-TDS must be applied for each pump time delay. Moreover, usually the change of electric field is small, so more data need to be taken to increase the SNR. As an example, the time for measuring perovskite solar cell material in Ref. [24] is 15 days, and the laser stability is a big issue in this experiment. To solve this problem, a fast data collection OPTP system based on high repetition rate laser (RegA, repetition rate: 250 kHz) with a fast-scan delay stage is designed. The data taking process would be accelerated by the higher repetition rate, fast-scan delay stage and DAQ card, which allow us to resolve the signal of each pulse (see in Chapter 3). The time taken for one measurement is expected to be 1/5 of the previous setup. The setup will be built in my future work.

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