Synthesis, characterization and terahertz study of metal oxides

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SYNTHESIS, CHARACTERIZATION, AND TERAHERTZ STUDY OF METAL OXIDES

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Synthesis, Characterization and Terahertz Study of Metal Oxides

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Table of Contents

Table of Contents	iii
Abstract	vii
List of Tables	x
List of Figures	xi
Publications	xix
Chapter 1 Introduction	1
§1.1 Overview and Motivation	1
§1.2 Core Theme and Outline of Dissertation.....	8
Chapter 2 Experimental Methodology	12
§2.1 Synthesis of Metal Oxides	12
§2.1.1 Solid State Reaction	12
§2.1.2 Pulsed Laser Deposition (PLD)	13
§2.2 Characterization Techniques.....	16
§2.2.1 X-ray Diffraction (XRD)	17
§2.2.2 Atomic Force Microscope/Piezoresponse Force Microscope (AFM/PFM) .	21
§2.2.3 Scanning Electron Microscope (SEM)	24
§2.2.4 Energy-Dispersive X-ray Spectroscopy (EDS).....	26
§2.2.5 Superconducting Quantum Interference Device (SQUID)	27

§2.3.6	Physical Property Measurement System (PPMS)	29
§2.3	Terahertz Time–Domain Spectroscopy (THz–TDS)	31
§2.3.1	Generation and Detection of THz waves	33
§2.3.2	Experimental Setup	38
§2.3.3	Simple THz–TDS Data Analysis	41
Chapter 3 Polaronic Transport and Magnetic Properties of Ag- and Cu-doped ZnO Ceramics		48
§3.1	Introduction	48
§3.1.1	Zinc Oxide (ZnO)	49
§3.1.2	The effect of doping	50
§3.2	Experimental Details and Characterizations.....	53
§3.3	Electrical Transport Properties of Ag- and Cu-doped ZnO Ceramics.....	60
§3.3.1	Variable Range Hopping Mechanism	60
§3.3.2	Results and Discussions	62
§3.3.3	Summary	64
§3.4	Room Temperature Ferromagnetism (RTFM) in Ag- and Cu-doped ZnO Ceramics.....	65
§3.4.1	RTFM in Wide-Band Metal Oxides	66
§3.4.2	Results and Discussions	67
§3.4.3	Summary	71
§3.5	Magnetoresistance in Ag- and Cu-doped ZnO Ceramics	72
§3.5.1	Introduction to Magnetoresistance.....	73

§3.5.2	Results and Discussions	75
§3.5.3	Summary	78
Chapter 4 THz Conductivity of Ag- and Cu-doped ZnO Thin Films.....		80
§4.1	Introduction	80
§4.2	Sample Preparation and Characterizations.....	82
§4.3	Experimetal Details and Data Acquisitions.....	84
§4.4	Conductivity Models and Discussions	88
§4.5	Summary	94
Chapter 5 THz–TDS of BiFeO₃ Thin Films Grown on SrLaAlO₄.....		95
§5.1	THz Dielectric Properties of SLAO Substrate.....	95
§5.1.1	Introduction to SLAO	96
§5.1.2	Experimental Details and Data Acquisition	97
§5.1.3	Results and Discussions	99
§5.1.4	Summary	104
§5.2	THz Properties of BFO Thin Films.....	105
§5.2.1	Introduction to BFO Thin Films	105
§5.2.2	Sample Preparation and Characterizations	106
§5.2.3	Experimental Details and Data Acquisition	108
§5.2.4	Results and Discussions	110
§5.2.5	Summary	113

Chapter 6 Measureing the Magnetoelectric Coupling in BFO Thin Films by Utilizing Low-temperature Grown GaAs-based Auston Switch –	
Preliminary Work	114
§6.1 Introduction	114
§6.2 Sample Preparation and Characterizations.....	117
§6.3 Device Fabrication and Experimental Setup	120
§6.4 Dependence of Laser Pump Power and Applied DC Volatge	122
§6.5 Summary	124
Chapter 7 Conclusions and Future Work	125
§7.1 Conclusions	125
§7.2 Future Work.....	127
Bibliography	130

Abstract

Title of Dissertation: SYNTHESIS, CHARACTERIZATION AND
TERAHERTZ STUDY OF METAL OXIDES

He Mi, Doctor of Philosophy, 2013

Dissertation directed by: Assistant Professor Chia Ee Min Elbert (supervisor)
Associate Professor Wu Tao, Tom (co-supervisor)
Division of Physics and Applied Physics

The interplays among various orderings of the spin, charge and orbital degrees of freedom in a broad spectrum of crystalline structures produce different forms of symmetry-breaking patterns of spatial inversion, time-reversal and gauge symmetries, leading to exciting emergent phenomena in strongly-correlated electron systems and promising a variety of potential applications. The main objective of this dissertation is synthesis, characterization and Terahertz (THz) study of metal oxides, which particularly refers to transition metal oxide of ZnO and multiferroic BiFeO₃ (BFO) materials. Systemic investigations of their physical properties as well as reasonable mechanisms not only deepen our understanding of interplays among those order parameters, but also shed light on the exploiting of value-added applications.

ZnO is one of the most important and versatile functional metal oxides in various forms of ceramics, thin films and nanostructures, due to its unique electrical, magnetic

and optical properties. Here, room temperature ferromagnetism has been achieved in ZnO bulk ceramics doped with nonmagnetic Ag and Cu elements. The percolation-based model of partially-ordered bound magnetic polarons plays the pivotal role in this weak ferromagnetism and its temperature dependence. Besides, the temperature dependent resistivity of undoped, Ag- and Cu-doped ZnO bulk ceramics are explained by Mott and Efros variable range hopping based conduction mechanism. As calculated from results of the Hall Effect measurement, all of samples are not weakly localized. Thus a semiempirical model combined by the positive and negative contributions is applied to fit the measured magnetoresistance at various temperatures. The positive contribution is described by a two-band model, while the negative contribution is expressed by the model considering the third-order expansion of the magnetic exchange Hamiltonian.

Besides, the optical response of undoped/doped ZnO in a new range of spectrum, named THz range, becomes very important. THz time-domain spectroscopic study of undoped, Ag- and Cu-doped ZnO thin films grown on z-cut quartz substrates provides the frequency dependent complex conductivity in the temperature range of 10 – 300 K. There is no absorption of THz pulse for the Cu-doped ZnO thin film, suggesting the sample is highly insulating and transparent of THz radiation. The measured complex conductivities of undoped and Ag-doped ZnO thin films are well fitted by the Drude-Smith model. When temperature increases, the extracted carrier density increases while the relaxation time decreases for the undoped ZnO thin film, but that for the Ag-doped ZnO thin film is not obvious. These results suggest our samples are in the localized regime.

On the other hand, BFO has attracted considerable interest recently due to its robust multiferroic properties with coexistence of both antiferromagnetic and ferroelectric

orders. Spectroscopic studies of lattice and magnetic excitations have been used to investigate its magnetism and ferroelectricity, as well as their coupling effect. Here, the THz response of the BFO thin film grown on the SrLaAlO_4 (SLAO) substrate is investigated by using THz time-domain spectroscopy. Firstly, the THz characterization of the as-grown and annealed SLAO substrates is performed. Their complex dielectric responses can be well described by the Lorentz model. The free carriers are reduced after the thermal annealing. The extracted complex refractive indices are used in the THz spectroscopic investigation of the BFO thin film. The enhanced conductivity could be ascribed to the domains in the BFO thin film. Also, the observed infrared E(1) mode and magnon modes are discussed.

Further, a novel ultrafast approach is presented which seeks to directly measuring the reversal rate (and hence the magnetoelectric coupling) by measuring the time-resolved magneto-optic Faraday and Kerr rotation (MOKE = magneto-optic Kerr effect). Based on this approach, LT-GaAs-BFO device is characterized, and fabricated by photolithography and Au wire bonding. Preliminary results show that the device is sensitive to the presence or absence of the incoming pump pulse. The measured current increases with increasing laser pump power and applied DC voltage. We did not see any pump–probe signal from the simple pump–probe experiment in reflection geometry ($\Delta R/R$). Next, we will take the measurement of time-resolved magneto-optic Faraday and Kerr rotation by using an amplified laser.

List of Tables

Table 3-1 Properties of Wurtzite ZnO.....	50
Table 3-2 Measured room temperature carrier concentration, mobility and the $k_F l$ value in Ag- and Cu-doped ZnO samples.	59
Table 3-3 Electrical transport fitting parameters in Cu-doped ZnO samples and carrier concentrations measured at 300 K.....	64
Table 5-1 Parameters obtained by fitting the experimental complex dielectric response of the as-grown and annealed SLAO substrate at 10 K.....	102

List of Figures

Figure 1-1 (a) A schematic illustration of different degrees of freedom and their interplays. (b) A variety of orderings in the ABO_3 perovskite materials induce a great number of functional properties: For instance, spins or electric dipoles are aligned cooperatively to form ferromagnetism or ferroelectricity, respectively; Charge transport leads to insulator-to-superconductor transitions, metal-to-insulator transitions, or colossal magnetoresistance. The green, blue and red spheres in the presented perovskite structure are the A, B, and O atoms, respectively. Figure taken from Ref. [1].....2

Figure 1-2 “Ferroelectricity in charge-ordered systems. Red/blue spheres correspond to cations with more/less positive charge. (a) Ferroelectricity induced by simultaneous presence of site-centered and bond-centered charge orders in a chain (site-centered charges and dimmers formed on every second bond are marked with green dashed lines). (b) Polarization induced by coexisting site-centered charge and $\uparrow\uparrow\downarrow\downarrow$ spin orders in a chain with the nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic couplings. Ions are shifted away from centrosymmetric positions by exchange striction. (c) Charge ordering in bilayered $\text{Lu}(\text{Fe}^{2.5+})_2\text{O}_4$ with a triangular lattice of Fe ions in each layer. The charge transfer from the top to bottom layer gives rise to net electric polarization. (d) Possible polarization induced by charge ordering and the $\uparrow\uparrow\downarrow\downarrow$ -type spin ordering in the a-b plane of perovskite of YNiO_3 .” Figure taken from Ref. [31].....6

Figure 2-1 (a) Schematic diagram and (b) photograph of a pulsed laser deposition apparatus.....15

Figure 2-2 (a) Photograph of a Bruker D8 Advanced Powder XRD. (b) Schematic illustration of interaction between X-rays and crystalline lattice, where the incident X-rays and the diffracted X-rays are symmetric to the normal of crystalline plane. (c) The diffraction peak is observed at the Bragg angle θ . The blue straight vertical line (delta function) represents the ideal peak for perfect

crystals and instrumentation. Figure taken from Ref. [51].	18
Figure 2-3 “Typical diffraction patterns for crystalline solids, liquids, amorphous solids, and monatomic gases as well as their mixtures.” Figure taken from Ref. [51].	20
Figure 2-4 (a) Schematic illustration of AFM and its work principle. (b) Photograph of a VEECO Dimensional-3100 AFM. (c) Diagram illustrating the forces between sample surface and probe tip, and the regimes for the three most common AFM modes. Figure taken from Ref. [54].	23
Figure 2-5 The principle of the SEM equipped with EDS (energy-dispersive X-ray spectroscopy) accessory. (a) Diagrammatic cross-section of the SEM. Figure taken from Ref. [60]. (b) Photograph of a JEOL JSM-6700F field emission SEM attached with EDS accessory. (c) Schematic representation of photon and charged particle emissions resulting from the interaction between electron beam and specimen surface. (d) Schematic diagram of the characteristic X-radiation under electron-specimen bombardment.	25
Figure 2-6 (a) Inner section of the MPMS where inside of the superconducting solenoid there are superconducting pick-up coils. Figure taken from Ref. [63]. (b) Photography of MPMSXL from SQUID Quantum Design. (c) Temperature dependent magnetization of YBCO thin film grown on the STO substrate shows its superconducting behavior as an illustration.	28
Figure 2-7 (a) The illustration of the probe cross section and its temperature control components. Figure taken from Ref. [64]. (b) Photograph of the PPMS.	30
Figure 2-8 Illustration represents the process of photoconductive THz generation. (a) The coplanar lines are DC-biased to form a static electric field. (b) The ultrafast optical pulse excites a number of charge carriers between the coplanar lines. (c) The static electric field accelerates charge carriers. (d) The accelerated charge carriers create an opposite an electric field. (e) A THz pulse is radiated as a result of the induced polarization. (f) Over a long time, the recombination of charge carriers makes the semiconductor substrate to the initial state. Figure taken from Ref. [75].	35
Figure 2-9 Illustration represents the process of photoconductive THz detection. (d)	

Top view of a Hertzian dipole antenna fabricated on the semiconductor substrate with side views in (a-c). (a) The optical pulse arrives before the THz pulse, corresponding to t_A in (e). (b) The optical pulse arrives when the THz wave propagates with its positive maximum, corresponding to t_B in (e). (c) The optical pulse arrives when the THz wave propagates with its negative maximum, corresponding to t_C in (e). (e) By adjusting the time delay between optical laser pulse and THz pulse, the THz field (or current) is mapped. Figure taken from Ref. [75].36

Figure 2-10 Setup of a TPS spectra 3000. (a) Schematic diagram of the setup, where the THz wave is generated and detected by photoconductive antennas. Figure taken from Ref. [101]. (b) Photograph of a commercial TPS spectra 3000. (c) Schematic illustrates the sample and reference mounted on the copper holder...39

Figure 2-11 Variation in focal spot size with frequency. Figure taken from Ref. [101].40

Figure 2-12 Transmittance amplitude spectra in the frequency domain after applying FFT show a high signal-noise ratio in the frequency window of 0.1 – 3.5 THz..41

Figure 2-13 Flow chart illustrates a typical process of the THz TDS data acquisition and analysis42

Figure 2-14 (a) Time-domain THz pulses transmitted through the c-Al₂O₃ and vacuum reference. (b) Amplitude spectra in the frequency domain after applying FFT. The inset shows the frequency dependent phase spectra.....43

Figure 2-15 Relations between the complex refractive index, conductivity and dielectric function for the c-Al₂O₃ single crystal in the frequency domain with the temperature of 10 K. A high-resistivity behavior is shown here.45

Figure 2-16 The refractive index and extinction coefficient are affected by the factors of temperature and structure orientation. (a) and (b) show the data of the c-Al₂O₃ single crystal in the temperature range of 10 K – 300 K. (c) and (d) indicate anisotropic THz properties of the a-Al₂O₃ single crystal, where the blue line

represents the data taken after rotating this sample by 90° in plane compared to the data in red line. The black line represents that of the α - Al_2O_3 single crystal. This set of data is taken at temperature of 300 K.46

Figure 3-1 (a) XRD patterns of $\text{Zn}_{1-x}\text{Ag}_x\text{O}$ samples. The data of undoped ZnO are also shown as reference. Dependence of lattice parameters (b) and unit cell volume (c) on the Ag concentration. The insets of (c) illustrate the onset of silver oxide clusters at higher doping concentrations. Figure taken from Ref. [116].54

Figure 3-2 (a) XRD patterns of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples. (b) Close-up of the (100) peaks, highlighting the shift with Cu doping. (c) Dependence of the lattice parameters and the unit cell volume on the Cu doping concentration obtained from the EDS results. Solid straight lines are guide for the eyes. Figure taken from Ref. [20]. ..55

Figure 3-3 (a) SEM image of Cu-doped ZnO sample with Cu concentration is 2% calculated from the EDS. (b-d) Corresponding Cu, Zn and O elemental mappings. It shows Cu is uniform doped without aggregation.55

Figure 3-4 The Hall resistivity vs. applied magnetic field in $\text{Zn}_{0.99}\text{Ag}_{0.01}\text{O}$ sample at temperature of 300 K, where the linear fitting (red line) gives the carrier type and concentration58

Figure 3-5 (a) Temperature dependent resistivity of the Ag-doped ZnO samples. (b) Data of $\ln\rho$ vs. $F(T) = [(T_{ES}/T)^{1/2} + (T_0/T)^{1/4}]$ for the Ag-doped ZnO samples. The solid straight lines are guide to the eyes. Figure taken from Ref. [116].....63

Figure 3-6 (a) Temperature dependent resistivity of the Cu-doped ZnO samples. (b) Corresponding resistivity vs. $T^{-1/2}$ curves. Solid straight lines are guide for the eyes.63

Figure 3-7 Magnetization (M) vs. applied magnetic field (H) data for Ag- and Cu-doped ZnO bulk samples at 300 K. (a) and (d) are the measured data on Ag- and Cu-doped ZnO samples, respectively. (b) and (e) are the corresponding ferromagnetic hysteresis loops after subtraction of the diamagnetic signal. (c) and (f) are enlarged views of the low field data.69

Figure 3-8 (a) Temperature dependent magnetization of the 2% Ag-doped and the 5%

Cu-doped ZnO samples measured under a magnetic field of 500 Oe. The magnetic transition temperatures are much higher than the limit of the oven attached to MPMS (780 K). Also shown are the theoretical fitting results (solid line) where partially ordered BMPs are assumed. (b) Illustration of two interacting magnetic polarons with localized carriers (hollow arrows) surrounded by magnetic impurities (solid arrows). The spins within the overlap region mediate the magnetic interactions. Figure taken from Ref. [116]. 70

Figure 3-9 (a) Magnetic field dependence of the MR effect for 2% Ag-doped ZnO bulk sample at different temperature. (b) Temperature dependence of MR at applied magnetic field of 5 T and 10 T, respectively. 76

Figure 3-10 Measured (solid dots) and fitted (solid lines) magnetic field dependence of the MR effect for 2% Ag-doped ZnO bulk sample at different temperature.... 77

Figure 4-1 Typical XRD patterns of Cu- and Ag-doped ZnO thin films grown on z-cut quartz, with undoped ZnO thin film as reference. 83

Figure 4-2 SEM images (cross-section view) and AFM images for undoped, Ag- and Cu-doped ZnO thin films. 83

Figure 4-3 (a) Time-domain THz pulse transmitted through the undoped ZnO sample and z-cut quartz reference at temperature of 10 K. (b) Amplitude spectra in frequency domain after applying FFT. 85

Figure 4-4 Amplitude of transmittance for undoped, Cu- and Ag-doped ZnO thin films at 10 K. The solid line represents the transmittance amplitude with both sample and reference referred to vacuum. The vertical dashed lines give the frequency window for further data analysis. 86

Figure 4-5 The refractive index (a) and extinction coefficient (b) of z-cut quartz with temperature range 10 – 300 K 87

Figure 4-6 Complex refractive indices of the undoped and Ag-doped ZnO thin films at temperature of 10 K and 300 K, respectively. 89

Figure 4-7 Complex dielectric functions of the undoped and Ag-doped ZnO thin films at temperature of 10 K and 300 K, respectively 89

Figure 4-8 Complex conductivity of undoped and Ag-doped ZnO. Solid lines represent the theoretical fitting results by applying the Drude-Smith model... 93

Figure 4-9 The fitting parameters (carrier density and relaxation time) of the undoped and Ag-doped ZnO thin films. They are extracted from the Drude-Smith model and plotted as a function of temperature.	94
Figure 5-1 (a) Time-domain THz pulses transmitted through the SLAO substrate and air reference. (b) Amplitude spectra in frequency domain after applying FFT. The inset shows the frequency dependent phase spectra.....	98
Figure 5-2 (a) Real and (b) imaginary parts of refractive index of SLAO substrate as function of frequency with different temperatures.....	100
Figure 5-3 Real and imaginary parts of complex dielectric response of SLAO substrate as a function of frequency, where the solid lines are fitting results.	101
Figure 5-4 The comparison of complex dielectric response for SLAO substrate before and after annealing, where the solid lines are fitting results.	103
Figure 5-5 Comparison of fitting parameters between as-grown SLAO and annealed SLAO as a function of temperature, where the black symbol is for as-grown SLAO and the red symbol is for annealed SLAO.	104
Figure 5-6 (a) High resolution XRD θ -2 θ scans of BFO thin film grown on the SLAO substrate. The blue symbols represent XRD peaks from the SLAO substrate. (b) Topographic AFM image. (c) In-plane PFM image. (d) Out-of-plane PFM image.	108
Figure 5-7 (a) Time-domain THz pulse transmitted through the BFO thin film sample and annealed SLAO reference at temperature of 10 K. (b) Amplitude spectra in frequency domain after applying FFT.....	109
Figure 5-8 Amplitude of transmittance for BFO thin film at 10 K and 300 K. The solid line represents the transmittance amplitude with both sample and reference referred to vacuum. The vertical dashed lines give the frequency window for further data analysis.....	110
Figure 5-9 Complex refractive indices of the BFO thin film grown on the SLAO substrate at various temperatures.....	112
Figure 5-10 Complex conductivity of the BFO thin film grown on the SLAO substrate at various temperatures.....	112
Figure 6-1 “Schematic layout of the magneto-optic experimental arrangement. The	

inset is the micrograph of microfabricated coil and sample. PD: photodiode, P1: polarizer, P2: Thompson polarizing beam splitter, BS1: 10% beam splitter, BS2: 50% beam splitter, PR: polarization rotator, DL: delay line, MO: microscope objective, DA: differential amplifier, PC: photoconductive switch, S1: GaAs substrate, S2: SiO₂ substrate, and V: bias voltage.” Figure taken from Ref. [280].

.....	115
Figure 6-2 Schematic of a pump-probe setup to measure the ME coupling in a multiferroic thin film.	117
Figure 6-3 (a) I-V curves of LT-GaAs shows Ohmic contact behavior with the applied voltage up to 200 V. (b) The resistance of LT-GaAs keeps stable for all applied voltages.....	118
Figure 6-4 (a) High resolution XRD patterns of BFO thin film grown on the STO substrate.....	119
Figure 6-5 Topography (a) and out-of-plane PFM (b) images of BFO thin film on STO substrate.....	120
Figure 6-6 (a) Autocad figure for the designed photomask. (b) and (c) SEM images show Au loops with different dimensions. (d) Photo of entire Auston Switch device. Compare this with Figure 6-6(a), the BFO grown on the substrate at the middle is light yellow, and the loops are fabricated on top of the BFO. The three large dark pieces surrounding the middle square are the Au electrodes deposited on LT-GaAs, where the fingers are located. Contacts were made using wire bonding. (e) “Fingers” of the Auston Switch where the pump pulse hits, (f) Blowup of one finger, showing clearly the gap between the fingers. The dark area is LT-GaAs, while the lighter area is the Au electrodes deposited on top of LT-GaAs.	121
Figure 6-7 Schematic (a) and photo (b) of the pump–probe experimental setup...	122
Figure 6-8 Resistance of the circuit in Figure 6-2. When the pump pluses impinges upon the Auston Switch, the circuit is closed, hence resistance approaches zero. When the pump pulse is blocked, the circuit is open, hence the circuit resistance increases to $\sim 10^9 \Omega$	123
Figure 6-9 Measured current as a function of laser pump power and applied DC	

voltage.	124
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1. G. Z. Xing, D. D. Wang, C. J. Cheng, **M. He**, S. Li, and T. Wu, “Emergent ferromagnetism in ZnO/Al₂O₃ core-shell nanowires: towards oxide spinterfeces”, *Appl. Phys. Lett.* 103, 022402 (2013).
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Chapter 1 Introduction

§ 1.1 Overview and Motivation

Oxides exist commonly on the surface of the earth in various forms and levels of technological sophistication, as a result of elements being oxidized by oxygen. An exciting research area in condensed matter science is the metal oxide, which plays host to a broad range of physical phenomena, ascribed to different degrees of freedom such as charge, spin, orbital and lattice, as well as the interactions among them. The interdependence of the material properties on the inherent complexity of the crystal structures, together with degrees of the freedom, have given rise to exciting research topics, such as superconductivity, multiferroics, spintronics, orbitronics, *etc.*, promising the development of cutting-edge technologies and value-added applications.

Metal oxides play an important role in the history of human society. It is accepted that pure aluminium foil is easily oxidized, but a thin coating of Al_2O_3 can prevent/reduce further corrosion, whereas the oxidation of another material, pure iron, hardly shows such functionality due to its different lattice structure. Such performances had been recognized and used by people during the early stage of human civilization. With the development of technology, researchers began to study the properties of materials, examine the possible mechanisms and design potential materials or applications. As we know, the core issue of metal oxides lies on the aforementioned degrees of freedom, which is illustrated schematically in Figure 1-1(a). Meanwhile the ABO_3 perovskites with related compounds as typical examples are shown in Figure 1-1(b), where the interplays among the spin, charge and orbital degrees of freedom endow those compounds with a variety of novel

emergent phenomena.¹

Figure 1-1 (a) A schematic illustration of different degrees of freedom and their interplays. (b) A variety of orderings in the ABO₃ perovskite materials induce a great number of functional properties: For instance, spins or electric dipoles are aligned cooperatively to form ferromagnetism or ferroelectricity, respectively; Charge transport leads to insulator-to-superconductor transitions, metal-to-insulator transitions, or colossal magnetoresistance. The green, blue and red spheres in the presented perovskite structure are the A, B, and O atoms, respectively. Figure taken from Ref. [1]

Take the spin degree of freedom as an example. In particle physics and quantum mechanics, spin is an intrinsic quantity resulting from angular momentum, and has both of magnitude and direction.² Spin has been studied for more than 100 years since the first milestone corresponding to Zeeman effect.³ An electron has typically two “characters”, one is charge and the other is spin, with spin direction ‘up’ or ‘down’. The arrangement of spins in the lattice structure with a certain space group could lead to the polarization of spins, resulting in magnetism as a macroscopic phenomenon. A special case is when the spin arrangement is geometrically frustrated, the spin glass/ice behavior can be observed and Ising model serves as the theoretical support. Neighboring spins can interact via an

exchange interaction without the need of an intermediary, called the direct exchange, whereas the indirect exchange means non-neighboring spins interact via an intermediary, such as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the double exchange interaction. Besides, electrons also have an orbital angular momentum, leading to a spin-orbital interaction according to Hund's rules.

Towards the end of the 1960s, researchers had begun exploring the potential technology by inducing spin functionality (magnetism, spin polarization) into the traditional semiconductor physics, whereas before, modern microelectronics mainly relies on charge functionality. Controlling the dopant effect provides a useful strategy to investigate application-worthy materials. Diluted spin doping induces novel properties into the parent materials with their main properties still being unaffected, e.g. the ferromagnetism has been demonstrated by measuring the magneto-transport in Mn-doped GaAs semiconductor matrix.⁴ The corresponding systems are broadly categorized as diluted magnetic semiconductors (DMSs), which promise potential applications in spintronics and have attracted considerable attention recently.

For decades, intense research efforts on DMSs have been done mostly in the following fields: (1). From the aspect of industrial applications, novel properties were pursued, where the major focus was on achieving high Curie temperature T_C as well as stable and intrinsic ferromagnetism in DMS materials doped with suitable dopants. Dietl and his colleges modified Zener's model to demonstrate ferromagnetism and predicted materials with room temperature ferromagnetism (RTFM).⁵ Now RTFM can be achieved in wide band-gap DMS materials (e.g. ZnO) easily by doping with different kinds of dopants, such as transition metals,⁶⁻¹¹ group I elements,¹²⁻¹³ group V elements,¹⁴ and so on,

since the first report of ferromagnetism in Mn-doped ZnO thin films.¹⁵ (2). Theoretically, the mechanisms behind such novel properties were elucidated. For example, when researchers tried to explain the occurrence of RTFM, several possible mechanisms were suggested, including RKKY, mean field theory, double exchange mechanism, and bound magnetic polaron (BMP) model. RKKY interaction was proposed 60 years ago, and described as a coupling mechanism of localized d or f shell electron spins by an interaction via the conduction electrons.¹⁶⁻¹⁸ This theory well explained the ferromagnetism in Mn-doped PbSnTe semiconductor,¹⁹ but not in transition metal doped ZnO system, as those d electrons are not exactly localized or itinerant. Based on RKKY interaction and Zener's model, Dietl *et al.* developed a mean-field theory to illustrate the ferromagnetism in DMSs, and the magnitude of T_C would be determined by the spin-orbit coupling in the valence band.⁵ However, this theory was unable to explain the ferromagnetism in DMS systems with low carrier density, as discussed in the previous reports.²⁰⁻²¹ Different from the long-range exchange in RKKY interaction, carrier-mediated double exchange mechanism described a short-range exchange interaction, which could contribute to the ferromagnetism in transition metal doped DMSs.²²⁻²³ Besides, BMP based model has been suggested where the overlap of percolated magnetic polarons yields ferromagnetism.²⁴⁻²⁵ Despite many experimental and theoretical investigations, the origin and control of ferromagnetism are still controversial research topics.

As one of the most investigated metal oxides in semiconductors, ZnO has been exploited in a variety of forms because of its unique properties, especially in nanoscale for new materials²⁶ and thin film heterostructures for device applications.²⁷ ZnO is a

typical II-VI semiconductor, with a direct wide-band-gap of 3.37 eV and large exciton binding energy of ~ 60 meV. Wurtzite is the thermodynamically stable phase for ZnO, which has a hexagonal crystal structure with space group P6₃mc. The unintentionally doped hydrogen, interstitial zinc (Zn_i), and/or oxygen vacancy (V_o), contribute to the native donor defects, leading to *n*-type doping with 0.01 – 0.05 eV below the conduction band.²⁸⁻³⁰ Doping various elements into ZnO can not only change the carrier concentration and type, but also modify the magnetic properties as well as the optical properties including photoluminescence, photoconductivity, absorption, *etc.* Besides, the non-centrosymmetric symmetry makes ZnO exhibit piezoelectric and pyroelectric properties. The broad range of excellent properties has generated corresponding application possibilities.

To achieve rich functionality, novel materials play a pivotal role in the exploration of potential materials and techniques, as they play host to a burst of physical properties based on degrees of freedom and their interactions. High dielectric permittivity, high temperature superconductivity, piezoelectricity and ferroelectricity are just some of functionalities metal oxides exhibit. Similar to magnetism which is from the ordering of spins in crystal structures, ferroelectricity is a result of relative shifts between the positive and negative ions with surface charges induced, as illustrated by Figure 1-2. Both magnetism and ferroelectricity show similar behaviors, such as the dependence of an external field, domain structures and anomalies at a critical temperature. Subsequently many efforts have been directed towards combining magnetism and ferroelectricity intimately in one material, though these two phenomena are mutually exclusive and weakly interact when they coexist.³¹ This brings multiferroics to the forefront of active

research, in the area of multifunctional devices.

Figure 1-2 “Ferroelectricity in charge-ordered systems. Red/blue spheres correspond to cations with more/less positive charge. (a) Ferroelectricity induced by simultaneous presence of site-centered and bond-centered charge orders in a chain (site-centered charges and dimmers formed on every second bond are marked with green dashed lines). (b) Polarization induced by coexisting site-centered charge and $\uparrow\uparrow\downarrow\downarrow$ spin orders in a chain with the nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic couplings. Ions are shifted away from centrosymmetric positions by exchange striction. (c) Charge ordering in bilayered Lu(Fe^{2.5+})₂O₄ with a triangular lattice of Fe ions in each layer. The charge transfer from the top to bottom layer gives rise to net electric polarization. (d) Possible polarization induced by charge ordering and the $\uparrow\uparrow\downarrow\downarrow$ -type spin ordering in the a-b plane of perovskite of YNiO₃.” Figure taken from Ref. [31].

Multiferroic materials have multiple degrees of freedom and offer an exciting coupling between electric and magnetic orderings. Magnetoelectric (ME) effect describes a phenomenon that an applied magnetic field can induce a dielectric polarization, or conversely an applied electric field can induce a magnetic moment.³²⁻³³ Early studies of

such ‘ME multiferroics’ languished around 1970s due to the mutually exclusion of both properties.³⁴ As summarized in Cheong and Mostovoy’s review, Figure 1-2 illustrated the ferroelectricity in charge-ordered systems.³¹ Most ferroelectric materials are transition metal oxides, where the empty d shells make the transition metal ions positively charged and subsequently cause a collective shift of anions and cations in a periodic crystal, contributing to the electric polarization. On the contrary, the transition metal ions with partially-filled d shells are needed for magnetism because the spins in fully-filled shells do not participate in the magnetic ordering. Further, improved first-principle calculations, and advanced techniques of thin-film growth, such as strain engineering and interface phenomena, modified the properties previously inaccessible by traditional chemical means. Thus interest on multiferroics has returned in the last ten years, and promised possible applications including data storage and switching devices, transducers, *etc.*

A remarkable example of multiferroic materials is bismuth ferrite, BiFeO_3 (BFO), because of its large polarization ($\sim 100 \mu\text{C}/\text{cm}^2$) and high Curie temperature ($\sim 1100 \text{ K}$). At room temperature, the ground state of bulk BFO is rhombohedrally distorted perovskite structure with space group $R3c$, and lattice parameters are $a_{\text{rh}} = 3.965 \text{ \AA}$ and $\alpha_{\text{rh}} = 89.4^\circ$.³⁵ The Bi^{3+} and Fe^{3+} cations are displaced along the $[111]$ threefold polar axis and off centered with respect to the barycenter of the oxygen polyhedra, contributing to a ferroelectric polarization along $[111]$.³⁶ Meanwhile, the Fe^{3+} magnetic moments are ordered ferromagnetically in the (111) planes and antiferromagnetically between adjacent planes. When the magnetic moments are perpendicular to the $[111]$ direction, a canting of the antiferromagnetic sublattices could result in weak ferromagnetism. The technique of thin-film growth provides ability to manipulate the lattice mismatch between films and

substrates, as well as the interface effect between the films of heterostructures, and thus drastically modifies the properties of materials. An example is the change of crystal symmetry when BFO thin films are grown on SrTiO_3 substrates, or the occurrence of orbital reconstruction between BFO and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films.³⁷⁻³⁸

Besides the transport investigations on this material, spectroscopic studies of lattice and magnetic excitations have been employed to investigate its magnetism and ferroelectricity. The measured absorption spectra of single crystal BFO revealed the optical band-gap of 2.67 eV at room temperature, due to the O $2p$ to Fe $3d$ charge transfer transition.³⁹ Raman, far-infrared and terahertz (THz) spectroscopic studies helped to unravel the magnetic excitations as well as the carrier dynamics in single crystal BFO.⁴⁰⁻⁴³ As mentioned before, the morphology of thin film modifies the properties of this material a lot, so such optical investigations on BFO thin films would unravel detailed mechanisms of magnetism and ferroelectricity, as well as the coupling effect between them.

§ 1.2 Core Theme and Outline of Dissertation

The interplays among various orderings of spin, charge and orbital degrees of freedom in a wide broad of crystalline structures introduce considerably exciting physical phenomena in metal oxides and promise a great deal of potential applications. Room temperature ferromagnetism and ferroelectricity are just a few of the functionalities exhibited by metal oxides. Systematic investigations of their typical properties as well as reasonable mechanisms not only enrich the phase diagram, deepen our understandings, but also make it possible to design new generation of devices and exploit value-added

applications. Based on this desire, the core theme of my dissertation is synthesis, characterization and THz study of metal oxides, which in particular refers to semiconductor of ZnO and multiferroic BFO materials. Such basic but vital studies help us to address several meaningful questions listed as follows:

RTFM has been achieved in ZnO doped with different dopants, but the mechanism is still controversial. Is it possible to achieve RTFM if ZnO is doped with nonferromagnetic dopants, such as group IB elements (Ag and Cu)? What is the possible mechanism of RTFM inside? What are the charge and magnetic transport behaviors when ZnO is doped with these dopants? Besides, ZnO is an excellent candidate for spintronic as well as optical devices. The optical response of undoped/doped ZnO in a new range of spectrum, named THz range, becomes important in order to enrich the physical understanding of materials and seek for the potential applications. The later aspect motivates us to further consider another key material, multiferroic BFO. Can THz spectroscopic study offer us insights into the principle of ferroelectricity and ME effect? What are the carrier dynamics of BFO thin films grown on different substrates, like the SrLaAlO₄ (SLAO) substrate?

In this dissertation, couplings among charge, spin, orbital and lattice in metal oxides have been investigated by mainly focusing on the transition metal oxide of ZnO and multiferroic BFO, whereas THz spectroscopy is an advanced technique that helps to unravel their optical properties. I consider this work as the start of further research more than a summary conclusion, as the subsequent design and study of functional materials, for instance, interfaces in heterostructures, give insight to the future in terms of fundamental physics and potential applications.

This dissertation is organized in the following manner:

Chapter 1 describes the background, motivation and objective of this study. With the purpose of investigating couplings between the spin, charge, orbital and lattice in metal oxides, I concentrate on the synthesis, characterization and THz study of typical metal oxide materials, e.g. the semiconductor of ZnO and multiferroic BFO. An overview of related work is also presented.

Chapter 2 introduces the approaches of synthesis and techniques of characterization. Conventional solid state reaction for ceramics and pulsed laser deposition for thin films are discussed firstly. In addition to a number of characterization techniques, the THz time-domain spectroscopy is described in detail, including the generation and detection of THz pulse, the experimental setup and the simple data analysis.

Chapter 3 discusses the polaronic transport and magnetic properties of Ag- and Cu-doped ZnO bulk ceramics. For charge transport, temperature dependent resistivity of undoped/doped ZnO samples were obtained, and was ascribed to the variable range hopping based mechanism. For magnetic behavior, weak ferromagnetism and its temperature dependence were explained using the percolation-based model of partially ordered BMPs. For magnetoelectric transport, a semiempirical model was considered to describe the measured magnetoresistance.

Chapter 4 provides the THz conductivity of Ag- and Cu-doped ZnO thin films grown on z-cut quartz substrates. Reasonable conductivity models including the Drude model, Drude-Smith model, and Drude-Lorentz model are proposed to describe the THz frequency dependent conductivity, and study the doping effect in ZnO thin films.

Chapter 5 investigates the THz response of BFO thin films grown on the SLAO

substrate. This project begins with suitable substrates for multiferroic complex oxide thin films and their THz responses. Because most thin film synthesis requires high temperature which unavoidably involves the annealing on the substrates, the effect of annealing on optical properties of SLAO substrate must be taken into account. After that, the THz response of the BFO thin film is evaluated.

Chapter 6 studies the magnetoelectric coupling in BFO thin films by utilizing a novel ultrafast approach. Low-temperature-grown GaAs was used to fabricate an Auston Switch, which was utilized in the optical pump–optical probe measurement to unravel the carrier dynamics as well as the magnetoelectric effect in BFO thin films. Preliminary results showed the response of the fabricated GaAs-BFO devices as a function of laser pump power and applied DC voltage. We did not obtain any pump–probe signal from the simple pump–probe experiment in reflection geometry ($\Delta R/R$) using a laser oscillator. We will next perform time-resolved magneto-optic Faraday and Kerr rotation by using an amplified laser.

Chapter 7 summarizes the whole dissertation and outlines future plans.

Chapter 2 Experimental Methodology

§ 2.1 Synthesis of Metal Oxides

Metal oxides show a sensitive dependence of novel properties on microstructure and morphology. Advanced techniques of synthesis provide pathways to access these novel property states, taking the study of metal oxides to a new level. Chemical doping, strain engineering and morphology control are just a few of routes to modify material properties and optimize their performance for applications. Numerous functionalities, such as the nanoscale effect, interface effect, and quantum effect, have been verified by applying different methods of synthesis. Here I will introduce conventional solid state reaction for ceramics and pulsed laser deposition for thin films.

§ 2.1.1 Solid State Reaction

Solid state reaction is the mostly widely used method to prepare polycrystalline metal oxides. In such reactions, atoms move through the crystal lattice to particular locations and react with their surroundings, producing the new compound. The kinetics of solid state reactions is largely dependent on the crystal structures, reaction conditions, surface area and thermodynamic free energy.⁴⁴ Also the phase diagram is important for determining the possible equilibrium. Normally solid state reactions take place at a temperature much higher than room temperature, which makes the reactions proceed at an appreciable rate.

A generally accepted model of solid state reaction is described here. After

considering the reaction conditions and the nature of reactants (usually metals or metal oxides), certain amounts of reactants are weighed in stoichiometric proportions and mixed together. The mixture needs to be grinded thoroughly, either manually by using an agate mortar and pestle, or automatically by employing a ball mill, to increase the surface area of reactants during reactions. Sometimes the volatile organic liquid (ethanol or acetone) is introduced during the process of grinding, which yields a homogeneous mixture. After that, the mixture is formed into a tablet through cold isostatic pressing, calcined and sintered in the high temperature furnace.

§ 2.1.2 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a highly versatile technique for the growth of thin films, where a high-power pulsed laser beam is used to ablate the target material, which is then deposited onto a substrate under a certain gas pressure.⁴⁵ Although PLD had its origin in the early 1960s when a ruby laser was introduced in the film deposition of semiconductors and dielectrics,⁴⁶ the real breakthrough was its application in the synthesis of high-temperature superconductor films in 1987.⁴⁷ Since then, PLD became popular and was widely employed in the growth of epitaxial, stoichiometric thin films on suitable substrates, where the produced thin films included simple materials, complex compounds and even multi-layer composites, such as colossal magnetoresistance materials, high-temperature superconductors, semiconductors, dielectrics, ferroelectrics, *etc.*

Figure 2-1 illustrates the principle of PLD process for the growth of thin films. Typically, an ultraviolet (UV) excimer laser with a pulse width of a few nanoseconds is

generated outside the chamber, goes through optical instruments, like lenses, mirrors and apertures, and focuses on the surface of target in the chamber. In general, the commercially available laser sources for PLD research have wavelengths ranging from 200 – 400 nm, high energy densities ($\sim 1 \text{ J/cm}^2$), and relatively large areas ($\geq 10 \text{ mm}^2$). Most of the deposition sources to date have been excimer and Nd^{3+} :YAG (yttrium aluminum garnet) lasers. The excimer is a gas laser system, with wavelengths in the UV range, such as XeF (351 nm), XeCl (308 nm), KrF (248 nm), KrCl (222 nm), ArF (193 nm), and F2 (157 nm). The pulse repetition rates can be high up to several hundred hertz (Hz) with energies near 500 mJ/pulse. The Nd^{3+} :YAG lasers are solid-state systems. The neodymium (Nd) ions pumped with the help of flashlamps or laser diodes cause a fundamental emission at 1064 nm, which are amplified by two YAG rods. Using a nonlinear crystal, the laser at 532 nm with about half power conversion efficiency is achieved, and with further mixing with the residual 1064 nm laser, produces final outputs of 355 nm or 266 nm, and pulse repetition rates limited to 30 Hz and energies up to 2 J/pulse. Besides, the laser beam can be in form of raster, or the target itself can be rotated, which achieves a uniform wearing of the target. The induced laser pulse is strong enough to ablate the target materials into atoms, electrons, ions, molecules, clusters, and molten globules, which form an energetic plasma plume.⁴⁵ Under appropriate conditions (background gas, pressure, target-to-substrate distance, growth temperature, *etc.*), such a plume moves forward, deposits on the substrates, and finally forms the desired thin films according to the thermodynamics, which is related to the surface energies of films as well as substrates, and their interface energy.⁴⁸⁻⁴⁹

Figure 2-1 (a) Schematic diagram and (b) photograph of a pulsed laser deposition apparatus.

Compared to the hardware as shown in Figure 2-1, the laser–target interaction is much more complicated. The mechanisms related to material ablation depend on laser characteristics as well as the properties of target materials, and can be described by two types of general mechanisms. The primary mechanisms include collisional sputtering, electronic sputtering, thermal sputtering, exfoliation sputtering, and hydrodynamic sputtering, while the secondary mechanisms involve outflow with reflection, effusion with reflection, and effusion with recondensation.⁴⁵ The principle sputtering mechanism in PLD is electronic sputtering, which involves a group of processes in some form of excitation and ionization. Besides, thermal sputtering is also important only if the target temperature is sufficiently high.

As one of the premier thin-film deposition technologies, PLD possesses a number of advantages over conventional deposition processes. Firstly, the employed UV laser pulse can be absorbed virtually by most materials via linear or nonlinear processes, and the independence of relation between laser pulse and target material makes such an energy source ubiquitous. Secondly, removing materials by stoichiometric means from a target

and reproducing on a substrate under appropriate conditions stand out as one of key features for PLD. Thirdly, the out-manipulation of laser source, the background gas and pressure in the chamber, the multiple targets loaded before deposition, the controlled temperature of film growth, and so on, provide a significant degree of parameter freedom for PLD process. However, major disadvantages like particulates and non-uniform thickness of produced thin films in large-area deposits still exist, though people have been trying to solve such deficiencies. That is also the reason why PLD technique is more popular in the laboratory researches rather than in industrial applications.

There are two sets of PLD apparatus employed in my experiments, with the same type of chamber. Excimer gas laser, which has a wavelength of 248 nm, is employed in the film growth of multiferroics and superconductors. The maximum pulse repetition rate is 20 Hz with energy high to 480 mJ/pulse. The base vacuum of PLD chamber is around 2×10^{-4} Pa, and during PLD process we could inject ambient gas to achieve the appropriate pressure. Also, the substrate can be heated to high temperature, around 780 °C. Self-rotation of the target and substrate holders makes the produced thin films very uniform. The set of PLD apparatus used in the film growth of ZnO-based semiconductors is similar to the previous one, except the main difference of laser source, where the latter involves a Nd³⁺:YAG solid-state laser, whose wavelength is 355 nm. Discussions about detailed growth parameters for different thin film materials will be presented in the following chapters.

§ 2.2 Characterization Techniques

In scientific studies and industrial applications, it is very important to identify and

characterize the synthesized ceramic, thin film, or nanostructure materials, which include the chemical compositions, lattice structure, purity, morphology, and so on. Many advanced techniques have been employed in the modern science and technology, with great revolutions as a result. In this section I will give a brief introduction on some of the widespread characterization techniques for synthesized materials.

§ 2.2.1 X-ray Diffraction (XRD)

X-ray Diffraction (XRD), a non-destructive analytical technique, reveals information including the crystalline phase, the lattice parameter, the chemical composition, and the grain size.⁵⁰ X-rays are discovered by Wilhelm Conrad Rontgen in 1895 (who received the Nobel Prize for Physics 6 years later). X-ray technology is commonly adopted in the medical diagnoses and treatments. The phenomenon of XRD was discovered by Max von Laue in 1912. For such applications, hard X-rays with wavelength from 10 Å to 0.1 Å are used as their wavelength is similar to the range of interatomic spacing in crystals. The wavelength λ (in Å) has a relation with photon energy E (in eV) in the formula: $\lambda = 12398.4/E$.⁵¹

Generally, X-rays can be generated from synchrotron radiation and X-ray tubes. The primary X-ray source, which is usually used in laboratory X-ray instruments, is generated by the X-ray tube, where a focused electron beam is accelerated by applying a high voltage field and bombards a solid target. Common targets like Cu and Mo are used with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively. On the other hand, synchrotron radiation is emitted by high-speed electrons or positrons and much more intense than that of X-ray tubes, which has brought advances in a number of structural

investigations.

Figure 2-2 (a) Photograph of a Bruker D8 Advanced Powder XRD. (b) Schematic illustration of interaction between X-rays and crystalline lattice, where the incident X-rays and the diffracted X-rays are symmetric to the normal of crystalline plane. (c) The diffraction peak is observed at the Bragg angle θ . The blue straight vertical line (delta function) represents the ideal peak for perfect crystals and instrumentation. Figure taken from Ref. [51].

Primarily X-rays interact with electrons in atoms. When an X-ray beam collides with electrons of a sample, besides the absorption and other phenomena, it will be deflected away from its original direction. If the wavelength of scattered X-rays is the same as that of the incident beam, an elastic scattering or coherent scattering occurs. Such scattered X-rays can be described in the intensity and spatial distribution, which forms a unique diffraction pattern according to the sample structure. Among various descriptions on the relationship between the diffraction pattern and the sample structure, Bragg law is the most comprehensive mechanism considered. As illustrated by Figure 2-2(b), the incident X-ray hits the atomic planes and then is scattered, with a same angle θ . Only by satisfying the Bragg condition, there diffraction peaks will occur:

$$n\lambda = 2d\sin\theta$$

where n is an integer determined by the order of reflection, λ is the wavelength of X-rays, d is the distance between each adjacent atomic planes (d -spacing), θ is the Bragg angle at

which a diffraction peak can be observed. Since a single wavelength is used in XRD, the Bragg equation is usually expressed with $n = 1$ because the effect of higher-order reflections is the same as that from different atomic planes. Figure 2-2(c) displays a typical diffraction peak denoted with two significant factors, the maximum intensity of the peak ($I_{\max}$) and the full width at half maximum (FWHM) which represent imperfect crystal conditions and instrumental conditions. In addition to the crystalline materials with long periodicity, XRD also provides information on the arrangement of atoms in materials, such as gases, liquids, and amorphous solids. Figure 2-3 compares different diffraction patterns schematically for crystals, liquids, monatomic gases, and amorphous solids as well as their mixtures.

There are different kinds of XRD techniques developed for various applications. Perhaps, powder XRD is the most common method for characterizing materials, and especially identifying unknown substances by comparing the acquired pattern to a standard pdf database (International Centre for Diffraction Data). Besides, the grain size of powder crystals can be calculated by applying the Scherrer equation:

$$\tau = K\lambda/\beta\cos\theta$$

where τ is the mean size of crystalline domains, K is the shape factor with a typical dimensionless value of ~ 0.9 , λ is wavelength of the X-ray, β is FWHM value, and θ is the Bragg angle. Compared with powder XRD, High-resolution XRD is the advanced version where much smaller divergence is achieved. Take Rigaku Smartlab high-resolution diffraction system as an example, which is used in my experiment. An incident beam with angular divergence less than 5 arc seconds is used by applying Ge monochromators. It provides kinds of powerful measurement packages available for θ - 2θ scan and ϕ scan,

X-ray reflectivity, glancing incidence diffraction, pole figure, rocking curve and reciprocal space mapping measurements. Therefore, various structural information of the investigated sample is obtained including crystallographic structure, epitaxial quality, thickness, roughness, structural and residual stress, texture, and so on.

Figure 2-3 “Typical diffraction patterns for crystalline solids, liquids, amorphous solids, and monatomic gases as well as their mixtures.” Figure taken from Ref. [51].

§ 2.2.2 Atomic Force Microscope/Piezoresponse Force Microscope (AFM/PFM)

Atomic force microscope (AFM), referred as part of a larger family of instruments termed the scanning probe microscopes (SPMs), is a versatile tool to image the sample surface in three-dimensional topography and manipulate matter on the sample surface, with a high resolution around the atomic scale.⁵² It was first described as a new technique by Binnig *et al.* to measure the surface of ceramic Al_2O_3 ,⁵³ and now has opened new perspectives in the investigation of material science, especially in the areas of biomedical and nanoscale materials, by “looking” at the sample with new “eyes”.⁵⁴ The basic idea of AFM is detecting the forces between the sample surface and the probe tip when the probe tip interacts with the surface directly. That offers AFM some advantages compared with electron microscope technology, such as the requirements of samples (the sample can be conductive/nonconductive in large scales) and environments (AFM can operate in fluid or air rather than in high vacuum).

AFM is performed based on the simple principle of examining the repulsive and attractive forces between the probe tip and the sample surface via incorporating some refinements, as shown in Figures 2-4(a) and (b). These refinements include flexible cantilevers, very sharp tips, a laser diode, a sensitive deflection sensor and high resolution tip-sample positioning. The core of AFM is the sharp tip (typically 20 nm), which is mounted at the end of the microcantilever to bring in closest interaction with the sample surface. Typically silicon or silicon nitride are used to fabricate the tip-cantilever assembly with sharp apex because of their high suitability of mechanical properties.⁵⁵⁻⁵⁶

Cantilevers are designed in “V” shape or single-arm shape, and essentially classified by their force constant and resonance frequency for different purposes. Opposite to the tip, a thin metal layer is coated on the upper surface of the cantilever to make it reflective surface, which is used to reflect the incident laser beam onto a position-sensitive photodetector. A piezocrystal is mounted upon the cantilever chip referred to the movement in z-axis direction. Thus with the probe scanning over the sample surface, a topographic image is achieved containing the information of height, force, phase and so on.

Generally, there are two operation modes for the AFM, named static mode (DC mode) and resonant mode (AC mode). They are easily distinguished depending on the absence or presence of the cantilever which oscillates in the proximity of its resonant frequency, or depending on the sign of forces between probe tip and sample surface. Figure 2-4(c) depicts the force regimes where the main mode operates. DC modes contain the contact mode (constant force mode), deflection or error mode, and lateral force mode, while AC modes include noncontact mode, intermittent contact mode (tapping mode), phase imaging mode, and force modulation mode.⁵⁷ By applying an appropriate mode, AFM has capability to investigate the materials’ structure, surface properties and interactive force at the meso- and nanoscale level.

In addition to the conventional AFM, various advanced modes and applications have appeared for the specific purposes due to scientific needs and developed technology. For example, magnetic force microscope (MFM) employs a magnetized cantilever to measure the magnetic momentum on the sample surface locally; conductive AFM (CAFM) employs a conductive probe tip to measure the electric potentials and conductance. Also,

Figure 2-4 (a) Schematic illustration of AFM and its work principle. (b) Photograph of a VEECO Dimensional-3100 AFM. (c) Diagram illustrating the forces between sample surface and probe tip, and the regimes for the three most common AFM modes. Figure taken from Ref. [54].

piezoresponse force microscope (PFM) can offer unique information on electromechanical coupling properties of piezoelectric, ferroelectric, biological and polymer materials. In the PFM mode, an external electric field can be established within the sample by applying a pre-set voltage between tip and surface when a conductive probe tip contacts with the sample surface. Because of the electrostriction, piezoelectric or ferroelectric materials would contract or expand locally under the electric field, which causes the decrease or increase of the cantilever deflection, and then demodulated by using a lock-in amplifier to obtain the local electromechanical properties of materials. The

common applications of PFM include mapping the detailed domains and investigating the domain switching dynamics, examining the electromechanical imprint, fatigue and dielectric break-down for electromechanical devices, electro-optical devices and nonvolatile memory components, *etc.*⁵⁸

§ 2.2.3 Scanning Electron Microscope (SEM)

As an electron microscope, scanning electron microscope (SEM) inspects the topographies of materials as well as displays the chemical compositions with a magnification range encompassing that of optical microscopes. It was first invented by Manfred von Ardenne in 1937,⁵⁹ and became a commercial instrument by Cambridge Instrument Company in 1964. Since then, it has been widely used in physical and medical sciences, especially in nanotechnology.

The SEM profiles a magnified image by using electrons. As schematically illustrated in Figure 2-5(a),⁶⁰ a beam of electrons (typical energy of 0.2 – 40 keV) is thermionically emitted by an electron gun, travels through a series of lenses within vacuum, and finally focuses on the specimen. The incident electrons interact with the specimen, and produce various photons and charged particles including characteristic X-rays, cathodoluminescence, transmitted electrons, auger electrons, backscattered electrons, and secondary electrons, as shown in Figure 2-5(c). These produced signals can be detected by different kinds of accommodated detectors which determine the specific abilities of a particular instrument.

Backscattered electrons and secondary electrons are most widely employed for imaging specimen. Secondary electrons have a low kinetic energy, less than 50 eV, with

Figure 2-5 The principle of the SEM equipped with EDS (energy-dispersive X-ray spectroscopy) accessory. (a) Diagrammatic cross-section of the SEM. Figure taken from Ref. [60]. (b) Photograph of a JEOL JSM-6700F field emission SEM attached with EDS accessory. (c) Schematic representation of photon and charged particle emissions resulting from the interaction between electron beam and specimen surface. (d) Schematic diagram of the characteristic X-radiation under electron-specimen bombardment.

their strength depending on the angle between the incident electrons and specimen surface.

Therefore, they can well show the morphology and topography of specimens. On the other hand, backscattered electrons have a high energy, with their strength depending on

the atomic number of the scattering elements.⁶¹ Thus they can describe the crystallographic structure of specimens by displaying contrasts in areas with different compositions.

Compared with the optical microscope, SEM has a better spatial resolution of a few nm, which depends on the wavelength of electrons, the electron-optical system and the specimen's interaction volume. One advantage of SEM is that the magnification can range from 10 to 500000 times by tuning the voltage of the x, y deflector plates or the current of the x, y scanning coils. In contrast to the AFM, the SEM requires the specimen to be conductive; otherwise a strong charging effect occurs on the specimen surface, resulting in a lower resolution. Usually it can be solved by coating a conductive film (like Au or graphite) on the specimen surface, though this method would induce contaminations.

§ 2.2.4 Energy-Dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) is an analytical capability to map the lateral elemental distribution of imaged areas or detect the elemental composition of individual points, by using a semiconductor detector to classify X-ray radiation based on energy rather than wavelength [N. B. Energy (keV) = $1.24/\lambda$ (nm)].⁶² It can be installed in the SEM and transmission electron microscope systems, where the high energy electron beams are used as the source. As described before, the accelerated electron beam bombards the specimen atoms, resulting in a verity of photons and charged particles produced. In this electron-specimen interaction, when electrons are ejected from the specimen atoms, which leads electron vacancies, the electrons located at a higher energy state will fill these vacancies accompanying with the emission of an X-ray as a result of

energy conservation, as illustrated in Figure 2-5(d). The unique electron orbital of the element makes the emitted X-ray with a characteristic energy. Thus the spectrum for each desired element is recorded by employing an EDS X-ray detector.

The accuracy of the EDS is affected by several factors, and its sensitivity to different elements plays an important role. Normally, the energy range of 1 – 10 keV is particularly useful in the EDS analysis, which contains K lines of elements with atomic number of 11 – 32, L lines of elements with atomic number of 30 – 80, and M lines with atomic number larger than 62. Elements with atomic number smaller than 5 are not able to be detected, like H, He, Li, and Be element. Besides, some overlapping peaks may exist in the spectrum due to the smaller energy difference compared to the resolution of the detector, like the K_α of Ti element and the L_α of Ba element.

§ 2.2.5 Superconducting Quantum Interference Device (SQUID)

Superconducting quantum interference device (SQUID) is a Josephson junctions employed device, which is very sensitive and able to measure the magnetic field. Josephson junction was theoretically proposed as a tunneling effect by B. D. Josephson in 1962, and experimentally performed by Anderson and Rowell in 1964. Due to its non-linear behavior and the Josephson quotient $2e/h$, the SQUID provides the ability to measure the change in the magnetic fields approaching 10^{-15} tesla.

Based on SQUID technology, the Magnetic Property Measurement System (MPMS) provides solutions for high sensitive magnetic measurement in many important areas, such as high-temperature superconductivity, magnetic semiconductor and biochemistry. The function of SQUID in the MPMS is not only a direct detector of the sample magnetic

field, but also a high sensitive current-to-voltage convertor. During one vertical scan, the sample moves upward from its initial position and through SQUID pickup coils, and a current is induced by the magnetic moment of the sample which would be converted to the output voltage regarding the sample's position.⁶³ Thus the output voltage variation is proportional to the current change, resulting from the magnetic flux change. From the measured raw data, we can investigate the magnetization and magnetic susceptibility of a sample.

Figure 2-6 (a) Inner section of the MPMS where inside of the superconducting solenoid there are superconducting pick-up coils. Figure taken from Ref. [63]. (b) Photography of MPMSXL from SQUID Quantum Design. (c) Temperature dependent magnetization of YBCO thin film grown on the STO substrate shows its superconducting behavior as an illustration.

In a fully calibrated MPMS, the measurement is usually taken several times to obtain the average at each position in the coils, which provides a highly accurate measurement. The calibration is performed on a palladium standard with known mass and magnetic susceptibility, and the shape is a circular cylinder, 3 mm in diameter $\times$ 3 mm in height. Such calibration can promise an accuracy of approximately 0.1%.

The experiment of magnetization measurement was carried out by SQUID Quantum Design, MPMSXL with MPMS MultiVu software, as shown in Figure 2-6. The sample parameters are 0 – 10000 g in mass, 0 – 9 mm in diameter and 0 – 100 mm in length. There are three types of standard sample measurement: Reciprocating Sample Option (RSO) measurement examines the magnetic moment of a sample by moving it sinusoidally and rapidly through the SQUID pickup coils. Unlike the RSO measurement, DC measurement stops sample movement for every reading by stepper motor. AC measurement has a resolution of $5 \times 10^{-12} \text{ A} \cdot \text{m}^2$ in the frequency range from 0.001 Hz to 1000 Hz, with loss of sensitivity happening when frequencies below 0.01 Hz. It has been widely applied to measure the magnetic susceptibility of materials with long relaxation time, e.g. spin glasses, or served as small excitation fields. In order to measure the magnetization at high temperature range, the MPMS Sample Space Oven is employed, which extends the temperature range to a nominal 800 K.

§ 2.2.6 Physical Property Measurement System (PPMS)

The physical property measurement system (PPMS) is an open architecture, variable temperature–field system, providing a flexible, automated work station for a variety of measurements, such as the magnetic, electro-transport, or thermal-electric transport. The

base system is a temperature, magnetic field and vacuum environment attached a sampling system and a helium gas control system, all controlled by PPMS MultiVu software. The temperature ranges between 1.9 – 400 K, and the magnetic field ranges between 0 – 14 tesla. By selecting different sample pucks and option apparatus, PPMS has been commonly adopted to measure resistivity, magnetoresistance, Hall Effect, heat capacity, thermal conductivity, AC susceptibility, DC magnetization, and so on. Low temperature of 0.35 K and 360 degree rotation are achieved by considering the helium-3 and horizontal rotator, respectively.

Figure 2-7 displays the PPMS and the cross section of the probe as well as its temperature control components.⁶⁴ The sample chamber locates inside of two vacuum tubes, and its base includes two thermometers, a heater and a 12-pin connector which is used to contact the installed sample puck. The diameter of PPMS sample chamber is 26 mm, much larger than 9 mm of MPMS, guaranteeing enough space for complex devices and electronic connectors. The region between the sample chamber and the inner vacuum

Figure 2-7 (a) The illustration of the probe cross section and its temperature control components. Figure taken from Ref. [64]. (b) Photograph of the PPMS.

tube is the cooling annulus, where the helium vapor flows at a certain rate achieving the temperature control. Normally the sample chamber is also filled with helium vapor with a pressure of a few torr, resulting in a thermal contact between walls of the sample space and the sample.

§ 2.3 Terahertz Time–Domain Spectroscopy (THz–TDS)

The terahertz (THz) region lies between far infrared (high-frequency optical side) and microwave radiation (low-frequency electronic side) in the electromagnetic spectrum, and initially was called as “THz gap” due to the few knowledge of nature and slow development of technology in the early stage. Pioneer THz radiation was carried out in the form of far-infrared (FIR) radiation by Ernest Fox Nichols and Heinrich Rubens in 1890s,⁶⁵⁻⁶⁶ whereas the modern THz spectroscopy came out of the research on Hertzian dipole antennae or electrical pulsed generated on transmission lines by Daniel Grischkowsky, David Auston and Martin Nuss in 1980s.⁶⁷⁻⁶⁹ Now it is attracting widespread interest in a number of fields such as security applications,⁷⁰ bio-medical imaging applications,⁷¹ nondestructive evaluations,⁷² telecommunications,⁷³ spectroscopic researches⁷⁴ and so on. Typically, 1 THz corresponds to a timescale of 1 ps, a wavelength of 300 μm , an energy content of 4.1 meV, a wave number of 33.3 cm^{-1} , and a chemical temperature of 47.6 K. From the aspect of time scale, the randomization of the carrier momentum due to carrier–phonon interactions usually occurs in (sub)picoseconds, and thus results to dispersion in the dielectric response on several meV from the aspect of energy scale. Therefore, THz time–domain spectroscopy (THz–TDS), as one of the most

important applications of THz radiation, offers a powerful means to investigate the THz frequency responses of various materials such as semiconductors, dielectrics, conductors, liquids, polymers, *etc.*

THz-TDS is a spectroscopic technique using femtosecond laser pulses to generate and detect the electromagnetic transients in the THz frequency range of 100 GHz – 10 THz. Comparing with other spectroscopic techniques, THz-TDS can directly measure the electric field including amplitude and phase because of its broad spectral bandwidth as well as the optically-gated detection. Thus the complex dielectric response or conductivity of the investigated materials can be examined without the Kramers-Kronig transformation.⁷⁵ Besides, an effective elimination of the thermal background promises the THz-TDS a relatively high signal-to-noise ratio even at room temperature. The modern technique of THz-TDS together with the particulars of THz radiation allow a fundamental study in the broad area of condensed matter physics, including the cooper-pair density in high-temperature superconductors,⁷⁶⁻⁷⁷ the conductivity of doped semiconductors,⁷⁸ the metal-insulator transition in colossal magnetoresistant manganites,⁷⁹ the dielectric response in multiferroics,⁸⁰ the charge trapping in polymer transistors,⁸¹ the anisotropic charge transport in carbon nanotubes,⁸² *etc.*

Due to the long THz wavelength, a poor spatial resolution limits the quality of THz imaging. Thus a number of efforts have been focused on surpassing the diffraction limit, such as the implement of near-field scanning optical microscopy.⁸³ By introducing ultrasolving THz near-field microscopy based on THz scattering at AFM tips, Huber *et al.* have achieved the highest resolution of $\lambda/3000$ at 2.54 THz.⁸⁴ Another major limitation of THz-TDS is its short THz frequency window, though where a high signal-noise ratio is

obtained (discussed later). Recently, new techniques of gas plasma on broadband THz generation and detection have been developed, which results in a much broader frequency window up to 30 THz. Here the THz emission from gas plasma is mainly explained by mechanisms of four-wave mixing,⁸⁵ asymmetric transient current⁸⁶ and quantum mechanical simulation;⁸⁷ whereas THz air-breakdown coherent detection (THz-ABCD) method is employed to detect the THz waves, which has been mainly developed by X. C. Zhang's group.⁸⁸

The rest of this section will focus on THz-TDS. Firstly, two most often used strategies (photoconductive and electro-optic methods) on the generation and detections of THz radiation are described. Followed are the detailed setup and operation of THz-TDS during my experiment. Finally I will cover the preliminary data acquisition and analysis, by taking the Al₂O₃ single crystal as an example.

§ 2.3.1 Generation and Detection of THz waves

Thanks to the development of ultrafast optical and electronic techniques, many of the technological difficulties for THz generation and detection have been overcome during the recent decades. Although there are a number of strategies to generate and detect the THz waves, the most often used by researchers are photoconductive and electro-optic techniques, as mentioned in the following content. Both of these two techniques involve a nonlinear interaction between the electric field and a material. However, the photoconductive technique is based on a resonant interaction which results to the absorption or destruction of the incident photons, while the electro-optical technique is relied on a non-resonant interaction where different frequencies mix via the optical

rectification.⁷⁵ Other techniques are also considered to generate and detect the THz waves. For example, THz waves can be emitted by intersubband transition in multiple quantum wells,⁸⁹⁻⁹⁰ charge oscillations between semiconducting quantum wells,⁹¹ Bloch oscillations in superlattices,⁹² or from the ionized air plasma.⁹³⁻⁹⁴

Photoconductive generation of THz waves occurs when a laser pulse optically excites the carriers of a semiconductor between two metal lines (bowtie or dipole structure also used) fabricated on it and thus causing a sudden conductivity change. Detailed processes are illustrated schematically in Figure 2-8. Generally, semiconductor substrates with high mobility, high electric breakdown field, low dark current, and ultrashort carrier lifetime are required for the photoconductive THz generation, like GaAs or low temperature-grown GaAs. On top of the substrate are fabricated with two coplanar transmission lines biased by a DC power supply (Figure 2-8(a)), which offers a high static electric field of 10^6 V/m. A optical pulse with energy higher than the bandgap energy of desired semiconductors is employed, and thus excites a number of electron-hole pairs near the semiconductor surface with absorption depth of $1/\alpha$, as shown in Figure 2-8(b). The excited electron-hole pairs accelerate to move oppositely under the high static electric field (Figure 2-8(c)), inducing a macroscopic polarization that opposite to the field in the semiconductor substrate (Figure 2-8(d)). The accelerated charge carriers which are formed by electron-hole pairs create a transient current, and according to the Maxwell's equations:

$$\begin{aligned}\nabla \times \vec{E}_{THz}(t) &= -\mu \frac{\partial \vec{H}_{THz}(t)}{\partial t} \\ \nabla \times \vec{H}_{THz}(t) &= \vec{J}(t) + \frac{\partial \epsilon(t) \vec{E}_{THz}(t)}{\partial t}\end{aligned}$$

Figure 2-8 Illustration represents the process of photoconductive THz generation. (a) The coplanar lines are DC-biased to form a static electric field. (b) The ultrafast optical pulse excites a number of charge carriers between the coplanar lines. (c) The static electric field accelerates charge carriers. (d) The accelerated charge carriers create an opposite an electric field. (e) A THz pulse is radiated as a result of the induced polarization. (f) Over a long time, the recombination of charge carriers makes the semiconductor substrate to the initial state. Figure taken from Ref. [75].

a THz field can be generated by the transient current (Figure 2-8(e)). After a long time, the charge carriers finally recombine to the initial state.

The principle of THz photoconductive detection is similar to that of generation, but without the biased DC voltage, as its process described in Figure 2-9.⁷⁵ A typical Hertzian dipole fabricated on the semiconductor substrate is used to detect the THz waves as

shown in Figure 2-9(d). An optical laser pulse incidents from the left side, and a THz pulse propagates from the right side but has not arrived yet (Figure 2-9(a)). Thus a number of electron-hole pairs are excited but move randomly, leading to no particular current direction. By adjusting the time delay of the incident optical pulse to the situation in Figure 2-9(b), where $t = t_B$, the excited charge carriers move oppositely under the electric field of THz wave, resulting to a particular current direction. The generated current flows through the dipole gap, and recorded by a high-sensitivity current amplifier. Therefore, similarly a time-domain electric field or current can be mapped by tuning the time delay between the incident optical pulse and the THz wave. Because the current typically relies on the carrier lifetime exponentially, to minimize the detector distortion, the carrier lifetime of the desired semiconductor should be less than half the temporal length of THz waves.⁹⁵

Figure 2-9 Illustration represents the process of photoconductive THz detection. (d) Top view of a Hertzian dipole antenna fabricated on the semiconductor substrate with side views in (a-c). (a) The optical pulse arrives before the THz pulse, corresponding to t_A in (e). (b) The optical pulse arrives when the THz wave propagates with its positive maximum, corresponding to t_B in (e). (c) The optical pulse arrives when the THz wave propagates with its negative maximum, corresponding to t_C in (e). (e) By adjusting the time delay between optical laser pulse and THz pulse, the THz field (or current) is mapped. Figure taken from Ref. [75].

A different approach for THz generation is optical rectification in inorganic electrooptic crystals, such as LiNbO_3 and LiTaO_3 , non-linear optical (NLO) crystals, such as GaAs, ZnTe, InP, *etc.*, or organic crystals, such as Poled-polymers, DAST (4-N, N-dimethylamino-4' -N' -Methyl stilbazolium tosylate), *etc.*⁹⁶⁻⁹⁹ When an ultrashort optical laser pulse incidents the NLO material, a polarization in the form of a power series is produced, where the second-order susceptibility term is responsible for the THz generation (inverse electro-optical effect). The short timescale of incident pulse makes the polarization dependent on the time-evolution, and thus determines the current or the emitted THz pulse in the time domain. This process can be understood in a frequency domain treatment, known as difference frequency generation, where the difference between all frequencies of an ultrashort pulse generates the overall spectrum of low-energy THz pulse. Different from the photoconductive THz generation, the electro-optical THz generation is a volume effect, so the NLO materials should be transparent to both THz and optical pulse, and their thickness becomes an important

parameter.

Inverse to the optical rectification, the electro-optical effect describes a refractive index change in NLO crystals caused by an electric field, which is also called Pockels effect and considered as the mechanism of THz detection by electro-optical sampling.¹⁰⁰ During this process, the THz electric field can induce birefringence in a NLO crystal by the Pockels effect, and this birefringence will cause the polarized optical pulse to rotate its polarization when it propagates the same NLO crystal. By controlling the overlap of THz electric field and optical pulse in the NLO crystals via mechanical delay stages, the THz electric field dependent birefringence as well as the polarization change is recorded, and thus the THz pulse is mapped in the time domain.

§ 2.3.2 Experimental Setup

Thanks to the unique insights that THz spectroscopy can provide into various areas as well as the increasing availability of commercial THz spectrometers, THz-TDS has been developed recently as a valuable technique widespread. In my experiment, the equipment used is TeraView's TPS spectra 3000, where its THz wave is generated and detected by photoconductive antennas fabricated on low-temperature-grown GaAs, as shown in Figure 2-10.¹⁰¹ Similar to other spectroscopic techniques, the desired THz radiation is generated in the photoconductive emitter, propagates through a sample, and then detected by a photoconductive receiver. A delay stage is employed in this system to map the THz signal in the time domain. The whole system is placed in a closed chamber purged with dry air to reduce THz absorption by water vapor.

The THz-TDS experiment is performed by comparing the transmitted THz spectrum

through a sample with that through a reference. Take 10 mm × 10 mm × 1 mm-thick Al₂O₃ single crystal (CrysTec GmbH, Berlin, Germany) as an example. The Al₂O₃ single crystal is attached to a copper holder and centered over a 7-mm-diameter hole in the plate, which defines the optical aperture (when the sample size is 5 mm × 5 mm, 3.5-mm-diameter aperture will be considered), as shown schematically in Figure 2-10(c). Another identical clear hole is used as a reference. By controlling the attached motorized linear stage vertically, the transmitted spectra of sample and reference are collected in turn. Besides, a continuous flow Helium-4 cryostat (or a closed cycle cryocooler), together with temperature controller is applied so that the temperature dependence of THz–TDS can achieve with temperature ranging from 5 to 310 K.

Figure 2-10 Setup of a TPS spectra 3000. (a) Schematic diagram of the setup, where the THz wave is generated and detected by photoconductive antennas. Figure taken from Ref. [101]. (b) Photograph of a commercial TPS spectra 3000. (c) Schematic illustrates the

sample and reference mounted on the copper holder.

Figure 2-11 Variation in focal spot size with frequency. Figure taken from Ref. [101].

Before the THz–TDS experiment, we examined the dynamic range of our THz–TDS system as well as requirements for the sample size. When the THz wave transmits a sample, its radiation is not homogenous but position-dependent. Generally, the energy distribution of high frequency radiation is located in the center of the aperture while the low one is broad. According to the diffraction-limited Airy disc size, 84% of the energy lies within a diameter: $2r = 2.44f\lambda/d$, where f , λ , and d are the focal length of the mirror, the wavelength of the radiation and the beam diameter at the sample focus optic, respectively. Figure 2-11 shows the variation of aperture with frequency. Thus the sample size is very important for the studies at the low frequency end of the THz spectrum. Moreover, the dynamic range and noise problem were examined by comparing the received THz signals while one transmitted through the aperture in vacuum and the other was blocked by the Cu plate. After Fast Fourier Transform (FFT), the transmittance

amplitude spectra in the frequency domain are plotted in Figure 2-12, where a high signal-to-noise ratio of $\sim 10^3$ can be obtained in the frequency window of 0.1 – 3.5 THz.

Figure 2-12 Transmittance amplitude spectra in the frequency domain after applying FFT show a high signal-to-noise ratio in the frequency window of 0.1 – 3.5 THz.

§ 2.3.3 Simple THz–TDS Data Analysis

In general, the THz–TDS data acquisition and analysis are straightforward, with a typical flow chart listed in Figure 2-13. In the THz–TDS experiment, the transmitted THz waveforms of both reference and sample are measured in the time domain. After FFT, these sets of data can be transformed to the corresponding amplitude and phase in the frequency domain, independently. Hence, the complex transmittance $\tilde{T}(\omega)$ is obtained as dividing the complex sample data $\tilde{E}_s(\omega)$ by the complex reference data $\tilde{E}_r(\omega)$. Depending on the experimental configuration, the complex transmittance $\tilde{T}(\omega)$ is derived as a function of the complex refractive index $\tilde{n}(\omega)$ of the sample as well as the

Figure 2-13 Flow chart illustrates a typical process of the THz-TDS data acquisition and analysis.

reference.¹⁰²⁻¹⁰³ Therefore, the frequency dependent complex refractive index $\tilde{n}(\omega)$ can be extracted numerically. Further, the frequency dependent complex conductivity $\tilde{\sigma}(\omega)$, the power absorption coefficient $\alpha(\omega)$, and the frequency dependent complex dielectric function $\tilde{\epsilon}(\omega)$ are obtained when considering the relations:

$$\tilde{n}(\omega) = n(\omega) + ik(\omega)$$

$$\alpha(\omega) = 2\omega k(\omega)/c$$

$$\tilde{\sigma}(\omega) \equiv \sigma_1(\omega) + i\sigma_2(\omega)$$

$$\tilde{\epsilon}(\omega) \equiv \epsilon_1(\omega) + i\epsilon_2(\omega) = [\tilde{n}(\omega)]^2$$

and,

$$\sigma_1(\omega) = 2n(\omega)k(\omega)\omega\epsilon_0$$

$$\sigma_2(\omega) = (\epsilon_\infty - n(\omega)^2 - k(\omega)^2)\omega\epsilon_0$$

$$\epsilon_1(\omega) = n(\omega)^2 - k(\omega)^2$$

$$\epsilon_2(\omega) = 2n(\omega)k(\omega)$$

where $n(\omega)$ is refractive index, $k(\omega)$ is extinction coefficient, ϵ_0 is permittivity of

free space (8.854×10^{-12} F/m), and ϵ_{∞} is high frequency dielectric constant. Moreover, with suitable models fitted on the THz frequency dependent results, the intrinsic physical properties of the investigated sample can be extracted, such as carrier concentration, the relaxation time, *etc.* The rest of this part will focus on the specific details by taking the Al_2O_3 single crystal as an example.

Figure 2-14 (a) Time-domain THz pulses transmitted through the c- Al_2O_3 and vacuum reference. (b) Amplitude spectra in the frequency domain after applying FFT. The inset shows the frequency dependent phase spectra.

The Al_2O_3 single crystal (c-cut) I measured here was commercially from CrysTec GmbH, Berlin Germany, with its size of 10 mm $\times$ 10 mm $\times$ 1 mm and optically two-side polished. As shown in Figure 2-10, before the measurement, the c- Al_2O_3 single crystal was attached to a copper holder and centered over 7-mm-diameter hole in the plate, which defines the optical aperture. Another identical clear hole was used as a reference, so the

complex refractive index ($\tilde{n} = 1$) of vacuum would be used. When each sample or reference ran, 900 THz scans were collected over 180 seconds. The transmitted electric field of THz pulses through the c-Al₂O₃ single crystal and the reference are recorded in the time domain, as displayed in Figure 2-14(a). The data analysis is performed on the main transmitted THz pulse because of the distinct separation between the main pulse and the etalon, which is contributed by multiple reflections between the front and back surface of the sample and exists after the main pulse. The corresponding amplitude and phase in the frequency domain can be obtained by applying FFT, as shown in Figure 2-14(b).

Subsequently, the frequency-dependent complex refractive index $\tilde{n}(\omega)$ can be extracted numerically without Kramers-Kronig relations, according to the equation:¹⁰²⁻¹⁰³

$$\tilde{T}(\omega) = \frac{\tilde{E}_s(\omega)}{\tilde{E}_r(\omega)} = \frac{4\tilde{n}(\omega)}{(1 + \tilde{n}(\omega))^2} \exp [i\omega d(\tilde{n}(\omega) - 1)/c]$$

where d is sample thickness. According to a series of related equations presented above, the relations between the complex refractive index, conductivity and dielectric function of the c-Al₂O₃ single crystal can be obtained, as displayed in Figure 2-15. It is clear shown that the refractive index n is ~ 3.06 with almost frequency-independent, and extinction coefficient k is ~ 0.001 indicating that the c-Al₂O₃ single crystal has no absorption feature in the THz frequency range. This feature is also indicated by examining the conductivity σ_1 and dielectric constant ϵ_2 in the THz frequency range. Typically, the complex refractive index is used for the representation of the dielectric properties when spectroscopic experiments are conducted. Sometimes the complex dielectric function is preferable due to its direct link between the applied electric field and the polarization. On the other hand, conducting materials are usually characterized by their complex

conductivity.

Figure 2-15 Relations between the complex refractive index, conductivity and dielectric function for the c-Al₂O₃ single crystal in the frequency domain with the temperature of 10 K. A high-resistivity behavior is shown here.

THz–TDS in the temperature range of 5 K – 310 K enhances its usefulness in the material investigation for a few reasons. First, we wish to study phase transitions above and below the transition temperature. Second, the coupling between electrons and other degrees of freedom is usually a strong function of temperature.^{41,104-105} Figures 2-16(a) and (b) present the refractive index and extinction coefficient of the c-Al₂O₃ single crystal

Figure 2-16 The refractive index and extinction coefficient are affected by the factors of temperature and structure orientation. (a) and (b) show the data of the $c\text{-Al}_2\text{O}_3$ single crystal in the temperature range of 10 K – 300 K. (c) and (d) indicate anisotropic THz properties of the $a\text{-Al}_2\text{O}_3$ single crystal, where the blue line represents the data taken after rotating this sample by 90° in plane compared to the data in red line. The black line represents that of the $a\text{-Al}_2\text{O}_3$ single crystal. This set of data is taken at 300 K.

at 10 – 300 K, which will be considered in the further thin film analysis where $c\text{-Al}_2\text{O}_3$ is used as substrate. Besides, the anisotropy because of a crystal asymmetry also plays a pivotal role in THz–TDS. For example, $\alpha\text{-Al}_2\text{O}_3$ has a hexagonal packed (hcp) lattice of aluminum atoms with the octahedral sites occupied by oxygen atoms.¹⁰⁶ Thus if the electric field is parallel to the c -axis of $\alpha\text{-Al}_2\text{O}_3$, isotropic THz properties can be obtained when this sample rotates in plane. But if the electric field is perpendicular to the c -axis of $\alpha\text{-Al}_2\text{O}_3$, obvious anisotropic THz properties can be obtained when rotating in plane, as

shown in Figures 2-16 (c) and (d). Therefore, we need pay attention to these effects when we take THz–TDS measurements.

Chapter 3

Polaronic Transport and Magnetic Properties of Ag- and Cu- doped ZnO Ceramics

As one of important and versatile functional metal oxides in a variety of forms including ceramics, thin films and nanostructures, ZnO is widely investigated and promises a broad range of the possible applications due to its unique physical (electrical, magnetic and optical) properties.^{27,107} Considering that factors like size effect for nanostructures, strain, substrate diamagnetism, and magnetic contaminations often lead to some properties which might not be intrinsic,¹⁰⁸⁻¹⁰⁹ so a systemic study is conducted on Ag- and Cu-doped ZnO bulk ceramic samples in order to unravel the underlying physics. This chapter starts with a general introduction of ZnO where the doping effect is discussed. Detailed sample preparation and characterizations are then given. Next, variable range hopping based conduction mechanism is suggested to explain the temperature-dependent resistivity. Room temperature ferromagnetism is examined, and instead of carrier-mediated mechanism, the percolation-based model of partially-ordered bound magnetic polarons play the pivotal role. A semiempirical model which combines the positive and the negative contributions of magnetoresistance is suggested to describe the behavior of magnetoresistance in Ag-doped ZnO bulk ceramic samples. Most of this work has been published in Applied Physics Letters **98**, 162503 (2011).

§ 3.1 Introduction

§ 3.1.1 Zinc Oxide (ZnO)

As a typical II-VI semiconductor, ZnO has a direct wide-band-gap of 3.37 eV and large exciton binding energy of ~ 60 meV, which makes it well suited to various applications. Among three types of crystal structures for ZnO, named rocksalt (B1), hexagonal wurtzite (B4) and cubic zinc blende (B3), the thermodynamically stable phase is wurtzite, which has a P6₃mc space group and lattice parameters $a = 3.296 \text{ \AA}$, $c = 5.207 \text{ \AA}$, respectively. The Zn atoms and O atoms are tetrahedrally coordinated, where the d electrons of Zn atoms hybridize with the p electrons of O atoms. Due to the alternately stacking of Zn^{2+} and O^{2-} ions, surfaces with a strong polarity along the c -axis can be obtained which lead to various nanostructures by surface reconstruction.⁶⁰ Besides, the non-centrosymmetric structure allows ZnO to exhibit piezoelectric properties.¹¹⁰ Intrinsically, ZnO is n -type semiconductor with energy band below the conduction band approximately 0.01 – 0.05 eV, which is contributed by the native defects and impurities as donors, like the oxygen vacancy (V_o), unintentionally doped hydrogen, and/or interstitial zinc (Zn_i).²⁸⁻³⁰ Moreover, ZnO exhibits excellent optical properties in the forms of absorption, photoconductivity, and photoluminescence, which demonstrates its intrinsic direct band gap, gap state resulting from defects, and bound exciton state. The observation of emissions in blue, green and near-UV regions could be explained by the self-activation of native defects.¹¹¹⁻¹¹³ The basic properties of ZnO are listed in Table 3-1,²⁷ and detailed database can refer to the Chapter 5 (ZnO) in the handbook on physical properties of semiconductors.¹¹⁴

Table 3-1 Properties of Wurtzite ZnO.

Property	Value
Lattice parameters at 300 K	
a_0	0.324 95 nm
c_0	0.520 69 nm
a_0/c_0	1.602 (ideal hexagonal structure shows 1.633)
u	0.345
Density	5.606 g/cm ³
Stable phase at 300 K	Wurtzite
Melting point	1975 °C
Thermal conductivity	0.6, 1–1.2
Linear expansion coefficient(/C)	$a_0: 6.5 \times 10^{-6}$ $c_0: 3.0 \times 10^{-6}$
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV, direct
Intrinsic carrier concentration	$< 10^6 \text{ cm}^{-3}$
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron Hall mobility at 300 K	200 cm ² /V s
for low n -type conductivity	
Hole effective mass	0.59
Hole Hall mobility at 300 K	5–50 cm ² /V s
for low p -type conductivity	

§ 3.1.2 The effect of doping

In semiconductor physics, doping is a typical method frequently used to modulate the properties with the purpose of realizing particular functionalities. By introducing various dopants, ZnO exhibits interesting electrical, magnetic and optical properties discussed as follows.

Naturally ZnO is n -type semiconductor as a result of its native defects. Both n -type and p -type ZnO are able to be obtained by doping certain dopants, where the carrier concentration also can be modulated. N -type doing can be easily obtained by doping

group III elements like In, Ga and Al, which would substitute the Zn element, or group VII elements like Cl and I, which would substitute the O element.¹¹⁵ Compared with *n*-type doping, *p*-type doping is not easy. One reason is that dopants may be compensated by low-energy native defects, and another reason is that dopants have a low solubility in host materials.¹¹⁵ Group I elements like Cu, Ag, K, Na and Li, and group V elements like As, P and N, are typical acceptors in ZnO from theoretical calculations, and may be possible for *p*-type doping.¹¹² But experimental results showed *n*-type doping in most cases, or unstable *p*-type doping which finally changed to *n*-type doping.^{20,116-118} Anyway, many efforts are still being contributed by researchers with the purpose of potential applications in the areas like device fabrication. Besides, the carrier concentration can be modulated by doping different elements, and the Ag- and Cu-doped ZnO discussed in this chapter is a good example.

The band gap can be modulated via doping. Normally, ZnO has a direct wide-band-gap of 3.37 eV. Literatures showed that the Cd substitution could lead a reduction of the band gap while the Mg substitution could increase the value of band gap, as the direct band gaps of CdO and MgO are 2.3 eV and 7.7 eV, respectively.¹¹⁹ Makino *et al.* demonstrated the band gap of $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ films was narrowed down to 2.99 eV with 7% Cd content.¹¹⁹ Ohtomo *et al.* achieved a band gap of 3.99 eV in Mg-doped ZnO with doping concentration is 33%.¹²⁰ When the crystal structure of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ changed from wurtzite to metastable cubic, the band gap of 5.0 eV could be realized.¹²¹ Besides, Co and Ni substitutions were also considered to tune the band gap of ZnO.¹²²

High-temperature ferromagnetism can be achieved in ZnO by doping. Since the RTFM was theoretically predicted,⁵ many efforts have been spent on exploring the effects

of doping on the non-magnetic metal oxides, aiming to lead to applications in spintronics and magneto-optics. The diluted doping introduces the spin functionality into the host material without affecting its original properties, thereby enabling the better usage of this material. Transition metals, like Ni, Co, Fe, Mn, Cr, Cu, and Ag, have been good candidates for ZnO doping, and RTFM was indeed reported in both bulk and films.^{107,123-124} Besides, RTFM also can be obtained in ZnO doped with other group elements, like Li, Na and K, *etc.*¹²⁻¹³ There are a number of mechanisms to explain the ferromagnetism in the doped ZnO system, but the origin still remains controversial.

ZnO exhibits interesting optical properties when doped with different kinds of elements, which promises potential applications in light emitting diodes, UV photodetectors, dye-sensitized solar cells, sensors and so on.¹²⁵ Cu-doped ZnO nanowires showed multiple absorptions in the ultraviolet and blue/green regions.¹²⁶ When Li was doped in ZnO as an acceptor, yellow luminescence band was demonstrated with a peak centered about 2.2 eV.¹²⁷ Red luminescence was also confirmed in Eu-doped ZnO nanowires.¹²⁸ Thereby, a wide range of the visible spectrum could be realized by employing ZnO doped with particular dopants.

In short, we can modulate the physical properties of ZnO via the method of doping, in order to achieve the desired applications as well as exploit the mechanisms underlying. Ag- and Cu-doped ZnO bulk ceramic samples will be studied in the remainder of this chapter. Theoretically, group IB elements (Au, Ag and Cu) are good acceptors and might contribute to ferromagnetism.^{8,11,129} Experimentally, the effects of this doping remain controversial and even the role of carriers is unclear. As Ag and Cu as well as the oxides are non-magnetic, Ag- and Cu-doped ZnO samples offer advantages in such an endeavor

compared to other compounds those may segregate into nanoscale magnetic precipitates and lead to extrinsic ferromagnetic signals. What is more, study on the bulk ceramic samples can avoid the factors including strain engineering and substrate diamagnetism, which often mask the weak ferromagnetism or even lead to artifacts. Based on this main motivation, we carried out the magnetic, electrical and magneto-electrical transport investigations of Ag- and Cu-doped ZnO bulk ceramic samples.

§ 3.2 Experimental Details and Characterizations

Bulk ceramic samples of Ag- and Cu-doped ZnO were synthesized by using a conventional solid state reaction. Take Ag-doped ZnO as an example. ZnO and Ag₂O powders (99.9%, Aldrich) were used to synthesize Zn_{1-x}Ag_xO (x = 0, 0.01, 0.02, 0.05, 0.08) bulk ceramic samples. The powders were weighed in stoichiometric proportions, mixed in a ball milling for 12 h, and then pressed into pellets by the cold isostatic pressing. Calcinations and sintering were performed in air at 1200 °C for 24 h, with intermittent grinding to enhance the uniformity. Similarly, ZnO (99.9%, Aldrich) and CuO (99.99%, Aldrich) powders were used to synthesize the Cu-doped ZnO bulk ceramic samples. During the sample preparation and further measurement process, only nonmagnetic tweezers and holders were used to avoid any magnetic contamination.

Figure 3-1(a) illustrates the XRD patterns of the Zn_{1-x}Ag_xO bulk ceramic samples, and the samples with doping concentrations lower than 5% show a pure ZnO phase (JCPDS No. 36-1451). As suggested previously,^{8,12,130} Ag ions are incorporated into ZnO at either the interstitial or the substitute sites. Samples with higher Ag concentrations show impurity peaks related to Ag or Ag dioxides, suggesting that the solubility of Ag in

ZnO is about 5%. The lattice parameters of $\text{Zn}_{1-x}\text{Ag}_x\text{O}$ samples are given in Figures 3-1(b) and (c). For the 1% and 2% Ag-doped ZnO samples, the lattice constant a slightly increases with the Ag doping while c increases more significantly, which gives an overall increase of the cell volume. This is because of the larger radius of Ag^+ ions (0.126 nm) compared to that of Zn^{2+} ions (0.074 nm). For 5% and 8% Ag-doped ZnO samples, both a and c decrease, which is consistent with the formation of nanoclusters.⁸

Figure 3-1 (a) XRD patterns of $\text{Zn}_{1-x}\text{Ag}_x\text{O}$ samples. The data of undoped ZnO are also shown as reference. Dependence of lattice parameters (b) and unit cell volume (c) on the Ag concentration. The insets of (c) illustrate the onset of silver oxide clusters at higher doping concentrations. Figure taken from Ref. [116].

Figure 3-2 illustrates the XRD patterns of the as-prepared $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples with Cu concentration of 1%, 2% and 5%. Further, the EDS results determine the Cu concentration as 0.5%, 1.2% and 2.8%, respectively (taking $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ as an example seen in Figure 3-3). From Figure 3-2, only the diffraction peaks according to the wurtzite ZnO phase appeared; the CuO secondary phase appears when the Cu concentration is higher than 5%, consistent with the previously reported low Cu solubility in ZnO.¹⁵ The (100) peak moves to higher angles as the Cu doping concentration increases (Figure 3-2(b)), suggesting a decrease in the lattice parameters. Our data also reveal a monotonous decrease of the unit cell volume, which reaches 0.3% at the highest Cu

doping (Figure 3-2(c)). Considering the relevant ionic radii of Cu^+ (0.60Å), Cu^{2+} (0.57Å) and Zn^{2+} (0.74Å), we conclude that a substantial amount of Cu ions substitute Zn in $\text{Zn}_{1-x}\text{Cu}_x\text{O}$.

Figure 3-2 (a) XRD patterns of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples. (b) Close-up of the (100) peaks, highlighting the shift with Cu doping. (c) Dependence of the lattice parameters and the unit cell volume on the Cu doping concentration obtained from the EDS results. Solid straight lines are guide for the eyes. Figure taken from Ref. [20].

Figure 3-3 (a) SEM image of Cu-doped ZnO sample with Cu concentration is 2% calculated from the EDS. (b-d) Corresponding Cu, Zn and O elemental mappings. It shows Cu is uniform doped without aggregation.

Due to the low solubility of Ag and Cu in ZnO, we focus on the 1% and 2% Ag-doped ZnO and 1%, 2% and 5% Cu-doped ZnO samples. The Hall Effect measurements are carried by PPMS, giving the room temperature carrier concentration (n) and mobility (μ) of the samples. As listed in Table 3-2, undoped ZnO exhibits a typical semiconductor behavior, while the doping of Ag leads to much higher carrier concentration, but lower mobility. Conversely, the doping of Cu results much lower carrier concentration.

In a disordered electronic system, the electronic wave function may be profoundly altered and even become localized if the randomness is sufficiently strong. That was firstly introduced by P. W. Anderson (1958), who proposed a quantitative estimate of the random potential strength to describe the absence of diffusion in certain random lattices.¹³¹ In 1968, Mott studied the localization related transport properties of amorphous semiconductors, where he introduced the mobility edge to separate the localized states from the extended states energetically.¹³² At the absolute zero of temperature, if only localized states exist near Fermi energy, they will not contribute to the transport, leading to the vanishing of DC conductivity, and thus the system will be an insulator. Oppositely, if the Fermi level lies in a region of extended wavefunctions, particles in such extended states can escape to infinity and contribute to the transport. Thus the DC conductivity will exist which makes the system to be metallic.

The disordered system can be described by a simple model with the tight binding Hamiltonian expressed as,

$$H = \sum_{jv} E_{jv} |jv\rangle \langle jv| + \sum_{jv,k\mu} V_{jv,k\mu} |jv\rangle \langle k\mu|$$

Here E_{jv} represents the energies at the j^{th} site of the lattice with v^{th} state, and the non-diagonal elements $V_{jv,k\mu}$ represent the matrix elements between the states. The potential energy corresponds to the diagonal part while the kinetic energy corresponds to the non-diagonal part.¹³³ The distribution functions for site energies are continuous in Anderson model, with formula,

$$p(E_{jv}) = \frac{1}{W} \Theta(\frac{1}{2}W - |E_{jv}|)$$

where width W is the magnitude of disorder. In this model, potential wells of varying depth are located on sites of a regular crystal lattice, and the overlap as well as the level dispersion can be fixed independently. Localization will be formed when the dispersion is much greater than the overlap. The asymptotic behavior of a localized state can be described by the exponential decay length of its envelope, known as the localization length λ ,

$$\psi(r) = f(r)e^{-\frac{r}{\lambda}}$$

and $f(r)$ is a randomly varying function. Based on this model, the metal-insulator transition in three dimensions and localization in one dimension were well predicted.

Different from Anderson localization, which shows an exponential decay of the vibration amplitude away from the main subregion, weak localization occurs with a slow decay of that due to the enhanced backscattering. In weak localization systems, the enhanced backscattering causes an interference of the electron wavefunctions, and thus results in the quantum corrections of the conductivity. Moreover, the localization length is considered to exceed all of other relevant lengths in this system.

In localization system, the transport only depends on the charge carrier hopping between localized states accompanying with the emission or absorption of phonon-like

Figure 3-4 The Hall resistivity vs. applied magnetic field in Zn_{0.99}Ag_{0.01}O sample at temperature of 300 K, where the linear fitting (red line) gives the carrier type and concentration.

excitations. Such hopping conduction can be examined by the temperature dependent behavior, which will be discussed later. Another characterization is the magnetic field dependence. By applying a magnetic field, a wavefunction would change its phase and thus change the interference of the quantum mechanical transport paths. As a typical result, the Aharonov-Bohm-like oscillations of the magnetoresistance occur in this disordered system, which was directly demonstrated in thin metallic cylinders by Sharvin *et al* (1981).¹³⁴ Another effect is the breaking of time-reversal invariance induced by a magnetic field, which leads to the metal-insulator transition. Further, with a strong magnetic field, the Hall conductivity of charge carriers at low temperatures can be quantized in units of e^2/h .¹³⁵

On the other hand, Hall Effect measurement by applying a magnetic field gives the carrier type as well as the carrier concentration for a disordered system. When the

Table 3-2 Measured room temperature carrier concentration, mobility and the $k_F l$ value in Ag- and Cu-doped ZnO samples.

Sample	n (cm ⁻³)	μ (cm ² /Vs)	$k_F l$
ZnO	3.4×10^{14}	3.35	9.85×10^{-5}
Zn_{0.99}Ag_{0.01}O	2.07×10^{19}	0.27	1.28×10^{-2}
Zn_{0.98}Ag_{0.02}O	9.74×10^{18}	0.13	3.84×10^{-3}
Zn_{0.99}Cu_{0.01}O	2.2×10^{11}	0.27	5.34×10^{-8}
Zn_{0.98}Cu_{0.02}O	6.36×10^{10}	1.17	1.09×10^{-7}
Zn_{0.95}Cu_{0.05}O	1.9×10^{11}	6.23	1.21×10^{-6}

scattering concentration is low, or the disorder potential is small, the electron wavefunction can be considered nearly plane-wave like, and thus the mean free path l is larger compared to the Fermi wavelength k_F^{-1} . That means in weak localization systems, the product of the Fermi vector k_F and the mean free path l would be larger than one.¹³⁶ Oppositely, in localization systems, the localized states near the Fermi energy are far from each other in space, leading to the hopping matrix exponentially small. Thus the product $k_F l$ value would be smaller than one.¹³⁶ So by calculating the product $k_F l$ value according to the equation,

$$k_F l = \hbar(3\pi^2)^{\frac{2}{3}}/(e^2 \rho n^{\frac{1}{3}})$$

we can examine a disordered electronic system in localization regime or weak localization regime. Here $\hbar$ is the Planck constant, e is the electron charge, ρ is the resistivity, and n is the carrier concentration. Ye. *et al.* calculated the $k_F l$ value for the superparamagnetic Zn_{0.95}Co_{0.05}O thin film which amounted to ~ 0.06 , suggesting the

sample was not in weakly localized regime, and thus a two band model was considered to describe the temperature dependent magnetoresistance behavior.¹³⁷ Xu *et al.* found the $k_F l$ value in Co-doped ZnO thin film system can be larger or smaller than one, depending on different deposition conditions.¹³⁸ For our Ag- and Cu-doped ZnO ceramic system, all of the calculated $k_F l$ values of the samples are smaller than 1, indicating the transport of the samples is in the localization regime.

§ 3.3 Electrical Transport Properties of Ag- and Cu-doped ZnO Ceramics

Undoped ZnO normally exhibits a semiconductor transport behavior, and is well explained by the band theory. In this band theory, the valence band is occupied by the energy states of electrons and the conduction band is empty. Between the bands is a forbidden energy gap (E_g) which is small that some electrons in the valence band still can jump to the conduction band via the thermal excitation, leaving the same amount of holes in the valence band. Such electrons and holes contribute to the conductivity of semiconductors, and thus the increasing temperature leads to an increased conductivity with a factor of $E_g/k_B T$.¹⁴² When the temperature is sufficient low that the thermal excitation is no longer suitable, the VRH mechanism is considered to describe the conduction behavior. In this part, we measured temperature dependent resistivity of Ag- and Cu-doped ZnO bulk ceramic samples via four-probe method in PPMS, with temperature range of 2 – 300 K.¹⁴³ The conduction mechanism as well as the doping effect will be discussed in details.

§ 3.3.1 Variable Range Hopping Mechanism

Variable range hopping (VRH) mechanism is usually and widely used to describe the low temperature conduction behavior in a strongly disordered system with localization states. Different from the relation of resistivity and temperature in the thermal excitation region, where $\rho(T) \propto \exp [E_g/k_B T]$ and the energy band gap plays an important role, VRH mechanism deals with the density of states at the Fermi level, where the hopping energy is much smaller than that in the thermal excitation. Thus, a universal relationship between resistivity and temperature is proposed by stretched exponents $\rho(T) \propto \exp [(T_0/T)^p]$ and the value of p represents one of the major three regimes such as the Mott ($p = 1/4$), the Efros-Shklovskii ($p = 1/2$) and the hard gap ($p = 1$) regimes.^{140,144-146} Generally, the VRH mechanism can well explain the electrical transport properties in doped crystalline and semiconductors theoretically and experimentally.

In 1968, Mott noted that a nonvanishing density of states located at the Fermi level would contribute to the hopping conduction when the temperature is sufficiently low. As a result, the resistivity exhibits temperature dependence with formula presented as: $\rho(T) = \rho_0 \exp [(T_M/T)^{1/4}]$, where T_M is Mott characteristic temperature related to the density of states at the Fermi level and the localization radius of states near the Fermi level.¹³² In 1970, Pollak pointed out that the density of states near the Fermi level would be reduced because of the electron-electron Coulomb interaction.¹⁴⁷ This ‘soft’ gap was experimentally observed by the photoemission and tunneling measurements.¹⁴⁸⁻¹⁵⁰ Efros and Shklovskii suggested that this gap dominated the hopping resistivity when the temperature is lower than that for the Mott VRH, and is of the form $\rho(T) = \rho_0 \exp [(T_{ES}/T)^{1/2}]$, where T_{ES} refers to the corresponding characteristic

temperature.¹⁵¹ A crossover between Mott and Efros-Shklovskii VRH regimes was also discussed.¹⁵² As the temperature decreases, the multiparticle excitations following the long-range electron hopping would become important and cause a deviation from the Efros-Shklovskii VRH. Therefore, the hard gap VRH was proposed to describe the temperature dependent resistivity, which exhibited a conduction behavior of simple thermal excitation, $\rho(T) = \rho_0 \exp [(T_H/T)]$.¹⁵³⁻¹⁵⁴ Here T_H is the characteristic temperature corresponding to the hard gap in the density of states near the Fermi level. Also, the crossover from Efros-Shklovskii to hard gap VRH with decreasing temperature had been studied in several materials, such as ion-irradiated polyimide films, ion-implanted Si: As samples and so on.¹⁵⁵⁻¹⁵⁶

§ 3.3.2 Results and Discussions

Figure 3-5 displays the resistivity versus temperature data of Ag-doped ZnO bulk ceramic samples. In the Figure 3-5(a), undoped ZnO shows a typically semiconducting behavior with the resistivity increasing dramatically when temperature decreases. While the resistivity of Ag-doped ZnO samples is several orders of magnitude smaller than that of the undoped ZnO, suggesting a significant amount of Ag^+ donors at the interstitial sites. The acceptors at the substitution sites appear to play a minor role in transport. The resistivity data of Ag-doped ZnO samples is shown in Figure 3-5(b), where the low temperature data cannot be explained by thermal activation across of a single band gap. Instead they fit well to the VRH mechanism which predicts $\ln \rho(T) \propto F(T) = [(T_{ES}/T)^{1/2} + (T_0/T)^{1/4}]$.¹⁵⁷ The first temperature dependent term comes from the Efros-Shklovskii VRH where the long-range Coulomb interaction localize carriers with

the corresponding characteristic temperature of T_{ES} . The second term is due to the Mott VRH with T_0 as the characteristic temperature. The hopping conduction confirms that the carriers are strongly localized and incapable to effectively mediate any magnetic exchange interaction.

Figure 3-5 (a) Temperature dependent resistivity of the Ag-doped ZnO samples. (b) Data of $\ln \rho$ vs. $F(T) = [(T_{ES}/T)^{1/2} + (T_0/T)^{1/4}]$ for the Ag-doped ZnO samples. The solid straight lines are guide to the eyes. Figure taken from Ref. [116].

Different from the conduction behavior of Ag-doped ZnO, Cu-doped ZnO show insulator-like transport behaviors with resistivity going up as temperature decreases, seeing Figure 3-6(a). Further, the linear relationship between $\ln \rho$ and $T^{-1/2}$

Figure 3-6 (a) Temperature dependent resistivity of the Cu-doped ZnO samples. (b) Corresponding resistivity vs. $T^{-1/2}$ curves. Solid straight lines are guide for the eyes.

Table 3-3 Electrical transport fitting parameters in Cu-doped ZnO samples and carrier concentrations measured at 300 K.

Sample	T_{Efros} (K)	ξ (Å)	r (Å)	n (cm ⁻³)
ZnO	3.9894×10^4	8.3768	24.5620	3.4×10^{14}
Zn_{0.99}Cu_{0.01}O	5.8862×10^5	0.5677	6.3940	2.2×10^{11}
Zn_{0.98}Cu_{0.02}O	6.3809×10^4	0.5237	6.1413	6.36×10^{10}
Zn_{0.95}Cu_{0.05}O	5.3922×10^4	0.6197	6.6804	1.9×10^{11}

[Figure 3-6(b)] suggests the Efros-Shklovskii VRH as the main conduction mechanism, meaning that Coulomb interactions between carriers dominate the electrical transport.¹⁵¹ The hopping resistivity can be described as $\rho = \rho_0 \exp (T_{ES}/T)^{1/2}$,¹⁵⁸ where $T_{ES} = (8e^2/\epsilon_r k_B \xi)$, ρ_0 is the resistivity coefficient, e is the electron charge, ϵ_r is the dielectric constant,²⁴ k_B is the Boltzmann constant, and ξ is the localization length of carriers near Fermi level. In addition, the optimal hopping distance is given by $r = (\xi/4) \times (T_{ES}/T)^{1/2}$. Table 3-3 is a list of fitting parameters. Previous Hall measurements indicated that the Cu doping significantly suppressed the electron concentration by at least three orders of magnitude, suggesting an effective compensation of the intrinsic n -type carriers. These very low carrier concentrations in Cu-doped ZnO samples also indicate the observed ferromagnetic order (which will be discussed in the magnetic investigation) cannot have a carrier-mediated origin.

§ 3.3.3 Summary

Temperature dependent resistivity of Ag- and Cu-doped ZnO bulk ceramic samples

is examined via PPMS. All these samples have *n*-type carriers which are strongly localized by calculating the product value of Fermi wave vector and mean free path. Ag-doped ZnO samples with doping concentration of 1% and 2% show higher carrier concentration compared with the undoped ZnO sample, which is consistent with their conduction behaviors. Mott and Efros-Shklovskii VRH are employed to describe their resistivity of temperature dependence. Whereas Cu-doped ZnO samples with doping concentration of 1%, 2% and 5% show lower carrier concentration compared with the undoped ZnO sample, agreeing with the measured conduction behaviors. Also Efros-Shklovskii VRH is applied to explain their resistivity of temperature dependence.

§ 3.4 Room Temperature Ferromagnetism (RTFM) in Ag- and Cu-doped ZnO Ceramics

Due to potential applications in spintronics, great attention has been attracted by DMSs recently as they can combine the capabilities of ferromagnetism and semiconductor properties in a single material. Following the observation of a ferromagnetic transition in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ with temperature excess 100 K,⁴ there has been a surge in studies where high temperature ferromagnetism was found in various semiconductor compounds theoretically and experimentally.^{107,159} Normally undoped ZnO bulk is a diamagnetic material.^{12,160} Since the initial theoretical prediction⁵ and experimental discovery¹⁶¹ of RTFM in ZnO-based DMSs, a variety of transition metal elements (Ni, Co, Fe, Mn, Cr and Cu) have been doped into ZnO and RTFM was indeed achieved in bulks, thin films and nanostructures.¹⁰⁷ Even for undoped ZnO, when prepared in nanostructures or thin films, its intrinsic defects like Zn and O vacancies and

interstitials could lead to RTFM.¹⁶²⁻¹⁶³ However, the mechanism of RTFM still remains controversial though there have been a number of reports on it.

Here we investigated the magnetic properties of Ag- and Cu-doped ZnO bulk ceramic samples by using MPMS attached with a high temperature oven. Unlike transition metal elements which tend to segregate into nanoscale magnetic precipitates and then lead to FM signals, all Ag, Cu and its oxides are nonmagnetic, which exhibits advantages in magnetic investigations. As to explain the measured magnetic results, we proposed a percolation-based model with partially ordered BMPs, where the Monte Carlo simulations well agree with the temperature dependent magnetization.

§ 3.4.1 RTFM in wide-band metal oxides

Since the initial theoretical prediction of ferromagnetism in wide-band metal oxides, the origin of ferromagnetism has been attracted much attention by researchers, which ensures the fulfillment of fundamental physics as well as the better control of spin functionality. Generally, there are two major types of mechanisms to explain the occurrence of RTFM: carrier-mediated based mechanism and BMP based model.

Carriers exhibit high importance to the origin of ferromagnetism in the carrier-mediated based mechanism. In this mechanism, the local magnetic spins are interacted by the mediation of conduction carriers, either in the form of long-range or short-range exchanges, and finally contribute to the ferromagnetism whose Curie temperature is mainly determined by the carrier concentration. Also the carriers in the value band could result to the ferromagnetism via the spin-orbit coupling. From this aspect, we could conclude that the requirement of high carrier density is indeed needed, in

order to the achievement of ferromagnetism. So usually it is not applicable to the system with low carrier concentration, as mentioned in Chapter 1.

On the contrary, the BMP based model offers an appealing opportunity to explain the ferromagnetism in the low-carrier-density systems like many of metal oxides. Conventional polarons are initially set forth in ionic or highly polar crystals, and described as composite particles which are made up of electrons and a cloud of virtual phonons surrounding the electrons.¹⁶⁴ Such phonons draw the positive ions toward the electrons and push the negative ions away. Analogously, magnetic polarons consist of the carriers with their spins together with the lattice magnetization created by the carrier spins. BMPs occur when the spins of the magnetic ions are aligned with that of localized carriers within a polariton radius, and an effective magnetic field is produced to make the spins aligned.¹⁶⁵ With temperature decreasing, the interaction distance grows and neighboring magnetic polarons may overlap and interact by the mediation of magnetic impurities. Thus, a transition of ferromagnetism occurs macroscopically.¹⁶⁶ In this BMP based model, even though the interaction of the neighboring localized carriers is antiferromagnetic, the interaction of BMPs may be ferromagnetic. Therefore, this BMP based model is inherently attractive.

§ 3.4.2 Results and Discussions

The magnetization (M) versus applied magnetic field (H) data measured on Ag- and Cu-doped ZnO bulk ceramic samples at 300 K are shown in Figures 3-7(a) and (d). The diamagnetic susceptibility of the undoped ZnO sample is -1.09×10^{-7} emu/g Oe, which is comparable to the earlier results.¹⁶⁷ The 1% Cu-doped ZnO sample also shows a

diamagnetic behavior. On the other hand, the 1% and 2% Ag-doped, as well as the 2% and 5% Cu-doped ZnO samples, show a ferromagnetic behavior besides the diamagnetic one. Figures 3-7(b) and (e) depict the ferromagnetic signals in Ag- and Cu-doped ZnO samples after deducting the diamagnetism. Figures 3-7(c) and (f) show the enlarged low field region of the hysteresis loops, which indicate the onset of RTFM. The saturation magnetization and the coercive field of the 2% Ag-doped and 5% Cu-doped ZnO samples reach 5.73×10^{-3} emu/g and 2.66×10^{-3} emu/g, 120 Oe and 37 Oe, respectively. This ferromagnetism is also verified by the temperature dependent magnetization data in Figure 3-8(a), where the magnetic signals of the 2% Ag-doped and 5% Cu-doped ZnO samples are sustained well beyond room temperature. The previous report suggests that CuO nanoparticles would result in ferromagnetism, but these hysteresis loops can be sustained only up to 330 K,¹⁶⁸ which is much lower than our results in Cu-doped ZnO samples. Therefore, we can conclude: first, the undoped ZnO bulk sample is diamagnetic,^{167,169} and the observed ferromagnetism cannot be contributed by its native defects alone; second, the observed ferromagnetism must come from the Ag or Cu doping which presumably modifies the magnetic exchange interaction.

Since the carriers in Ag- and Cu-doped ZnO bulk samples are strongly localized, and the Curie temperature is higher than room temperature, we hypothesize the percolation theory of BMP is favored to explain the observed magnetism.^{25,170} In a BMP, magnetic impurities within a correlation radius $r_{corr}(T)$ of the central bound charge carrier have their spins anti-aligned with the localized spin.¹⁷¹ At high temperatures, $r_{corr}(T)$ is small, and magnetic moments of the BMPs point in random directions, leading to a zero net magnetization. With decreasing temperature, $r_{corr}(T)$ increases, and BMPs start to

Figure 3-7 Magnetization (M) vs. applied magnetic field (H) data for Ag- and Cu-doped ZnO bulk samples at 300 K. (a) and (d) are the measured data on Ag- and Cu-doped ZnO samples, respectively. (b) and (e) are the corresponding ferromagnetic hysteresis loops after subtraction of the diamagnetic signal. (c) and (f) are enlarged views of the low field data.

overlap, producing an effective ferromagnetic interaction that aligns the magnetic moments of BMPs (see Figure 3-8(b)).^{25,172} As we lower the temperature further, more

and more BMPs overlap, and eventually a percolation threshold is reached, producing an overall magnetism.^{25,172}

Figure 3-8 (a) Temperature dependent magnetization of the 2% Ag-doped and the 5% Cu-doped ZnO samples measured under a magnetic field of 500 Oe. The magnetic transition temperatures are much higher than the limit of the oven attached to MPMS (780 K). Also shown are the theoretical fitting results (solid line) where partially ordered BMPs are assumed. (b) Illustration of two interacting magnetic polarons with localized carriers (hollow arrows) surrounded by magnetic impurities (solid arrows). The spins within the overlap region mediate the magnetic interactions. Figure taken from Ref. [116]

To fit our experimental data to the BMP percolation theory, it is assumed that magnetization of the sample is proportional to the size of the giant percolation cluster, which is a collection of overlapping spheres.¹⁷³ Furthermore, the high synthesis temperature leads to a partial ordering of the doped Ag and Cu, giving rise to partially ordered distribution of BMPs with small random displacements from a wurtzite superlattice. The parameters we used for our fits are the bound carrier concentration n_h , the maximum magnetization m_0 of a BMP (based on the concentration of magnetic impurities), the Curie temperature T_C , and the amplitude δ of the random displacements of BMPs from the wurtzite superlattice. To fit our experimental data to the BMP percolation theory, we start with initial guesses for n_h , m_0 , T_C , and δ . At each

temperature T , we ran Monte Carlo simulations with different BMP distributions, referring to the procedure in Ref. 166. We determine the largest cluster of overlapped BMPs in each simulation and average over 1000 simulations to obtain the theoretical magnetization $m(T)$. We compare this theoretical curve against the experimental data to find the best fit. As we can see from Figure 3-8(a), there is a good agreement between the BMP percolation theory and the experimental data, which gives strong support to the existence of BMPs in Ag- and Cu-doped ZnO bulk samples. We found a critical transition temperature of $T_C = 995$ K for 2% Ag-doped ZnO sample, with other parameters: $n_h = 3.403 \times 10^{15} \text{ cm}^{-3}$, $m_0 = 3.954 \times 10^{-3} \text{ emu/cm}^3$, $\delta = 8.007 \times 10^{-3}$. Thus, the concentration of bound polarized carriers ($3.40 \times 10^{15} \text{ cm}^{-3}$) derived from the fitting is much smaller than the result of Hall Effect measurement ($9.74 \times 10^{18} \text{ cm}^{-3}$), indicating that only a small portion of the carriers contribute to the ferromagnetism.

§ 3.4.3 Summary

Magnetization of Ag- and Cu-doped ZnO bulk ceramic samples is examined via MPMS with a high temperature oven attached. Undoped and 1% Cu-doped ZnO bulk samples show diamagnetic signal, while 1%, 2% Ag-doped and 2%, 5% Cu-doped ZnO bulk samples exhibit weak ferromagnetism with clear hysteresis loops at room temperature. Temperature dependent magnetization demonstrates that the Curie temperature is much higher than 780 K, which is the limit of MPMS. Such observed ferromagnetism in Ag- and Cu-doped ZnO bulk ceramic samples is intrinsic, with the Ag and Cu doping playing a pivotal role in establishing ferromagnetic order. Here, the percolation-based model of partially ordered BMPs is applied to explain the observed

ferromagnetism, and the fitting results of Monte Carlo simulations well agree with our experimental results. This percolation theory of BMPs hopefully can also be applied to other doped wide-band metal oxides and give insight on the ferromagnetic order.

§ 3.5 Magnetoresistance in Ag-doped ZnO Bulk Ceramics

The magnetoresistance (MR) of a material describes the change of its resistivity subjected to a magnetic field. Classically, the strength of the magnetic field and the relative direction between the magnetic field and the current flow determine the MR effect.¹⁷⁴ This MR effect has been well employed in various technologies, including the magnetic recording media with high-speed read/write heads and magnetic sensors.¹⁷⁵ Since the semiconductor industry has been well established, DMSs draw a large number of interests in the areas where functionalities of the electron charge and spin freedom can be modified. As discussed before, the effect of doping in wide band gap oxides gains great importance in the manipulation of various properties. Besides the conventional magnetic measurements, magneto-transport measurements, in particular MR, are effective to reveal the magnetic interactions in these doped materials. Although there have been a series of reports on the observed MR behavior, a thorough understanding in the mechanisms of this observed MR behavior is rather challenging, which could turn a new page on the origin of ferromagnetism.^{138,176-179}

Here we took 2% Ag-doped ZnO bulk ceramic sample (the MR behavior of 1% Ag-doped ZnO sample is similar) as an example to examine its MR effect by using PPMS with temperature ranging 10 – 300 K. The magnetic field was applied perpendicular to the

current flow up to 10 Tesla (T), and the MR was defined as $MR(H) = [R(H) - R(0)]/R(0)$, where $R(H)$ and $R(0)$ are the resistance of a material with and without an applied magnetic, respectively. The measured MR was elucidated by a semiempirical model which combining the mechanisms in the positive MR and negative MR, and the good consistency between theoretical and experimental results not only explains the origin of MR in Ag-doped ZnO sample, but also suggests that the magnetic exchange interaction of wide band gap oxides can be rational tailored by doping different transition elements. Besides, this semiempirical two band model is also suitable for Cu- and Co-doped ZnO thin film samples.¹⁸⁰

§ 3.5.1 Introduction to Magnetoresistance

Typically, there are four kinds of MR: ordinary magnetoresistance (OMR), anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR) and colossal magnetoresistance (CMR). OMR occurs in a normal material under an applied magnetic field, and due to the Lorentz force the trajectories of the electrons follow a helical motion, resulting in the increase of resistivity. This process leads to a small positive OMR of 1% under the magnetic field of 1 T and varies as B^2 in the low field regime.¹⁸¹ AMR was first discovered in ferromagnetic metals with anisotropic spin-orbit interaction by W. Thomson in 1857, who found a 0.2% increase in the resistance of Fe under a parallel magnetic field but a 0.4% decrease under a transverse magnetic field.¹⁸² Around 130 years later, GMR was discovered by Fert's group (Fe/Cr multilayer)¹⁸³ as well as Grunberg's group (Fe/Cr/Fe trilayer),¹⁸⁴ mainly thanks to the improvement in thin film deposition technologies. GMR is a quantum mechanical effect based on spin-dependent scattering

phenomena in magnetic multilayers, and can be described by a two fluid model of the conduction process. Different from GMR, CMR was discovered in $\text{La}_{1-x}\text{M}_x\text{MnO}_{3+\delta}$ ($\text{M} = \text{Ca}, \text{Sr}$) perovskite structures with a huge observed MR effect.¹⁸⁵ It occurs in the metal regime of a material, and the indirect exchange interaction, such as RKKY interaction, might be responsible for the conductivity.

Due to the distinguished feature of spin functionality in wide band gap metal oxides, their MR effects have been extensively investigated by many researchers, with a variety of mechanisms proposed to explain the observed MR. Here we introduce several different mechanisms to describe the related positive MR and negative MR in wide band gap metal oxides. The OMR normally leads to a positive MR, where the action of Lorentz force under a magnetic field increases the possibilities of collisions, and that could be demonstrated in Co-doped ZnO samples.¹⁷⁷ For materials such as CuInSe_2 , GaAs and CuGaSe_2 , positive MR can be resulted from the magnetic field induced shrinkage of carrier's wave function.¹⁸⁶⁻¹⁸⁸ Moreover, positive MR can be observed when spins in the conduction band split under interactions between carriers and doped magnetic moments, which has been demonstrated in Co-doped TiO_2 , Mn- and Co-doped ZnO samples.¹⁸⁹⁻¹⁹⁰ In this model, the conduction band will split into two subbands with opposite spin orientations in the presence of an applied magnetic field. Thus the electrons near Fermi level will transfer from the subband with high-energy to that with low-energy, resulting in the redistribution of electrons. Such electron redistribution increases the Thomas-Fermi screening radius and finally leads to the positive MR.¹⁹¹

Similarly, negative MR could be attributed to several models, where the most widely discussed is the formation of magnetic polarons (MPs). With this model, magnetic

moments around the localized carriers form MPs which cause the negative MR properties in the transition metal doped DMS system.¹⁹² A consistent semiclassical analysis as well as different kinds of experiments including spin-flip Raman scattering and neutron scattering have been reported to support the formation of MPs.¹⁹³⁻¹⁹⁴ Besides, the mechanism based on the quantum corrections on the effects of weak localization or electron-electron interactions could result in negative MR.¹⁹⁵ This weak localization based model usually illustrates the small negative MR in the low field regime. Anderson localization based scenario is also employed to explain the giant negative MR, such as that in Mn-doped GaAs samples.¹⁹⁶

§ 3.5.2 Results and Discussions

Figure 3-9(a) presents the magnetic field dependence of the isothermal MR effect of 2% Ag-doped ZnO bulk ceramic sample with the magnetic field applied perpendicular to the current flow. The observed MR effect does not show a typical “butterfly” MR loop, which is usually induced by spin-dependent hopping in ferromagnetic semiconductors.¹⁹⁷ Beside, it shows an unsaturated behavior even when the applied magnetic field reaches to 10 T. Comparing with the obvious hysteresis loops in the M-H curve, it is found that the MR curve does not turn to saturation though the magnetic moment does. That means there is no direct relation between the MR curve and the magnetization reversal. On the other hand, the MR effect strongly depends on the temperature, as displayed in Figure 3-9(b). The maximum value of positive MR can reach to 16% at 5 K with applied magnetic field of 10 T. This positive MR decreases rapidly with increasing temperature, and the negative MR can be observed at high temperature regime. The product of Fermi wave vector and

Figure 3-9 (a) Magnetic field dependence of the MR effect for 2% Ag-doped ZnO bulk sample at different temperature. (b) Temperature dependence of MR at applied magnetic field of 5 T and 10 T, respectively.

mean free path calculated from Hall Effect measurement is 0.0038, much smaller than 1, suggesting our sample is not in the weak localization regime.

In order to evaluate MR theoretically, a semiempirical model combining both the positive and negative contributions is considered here. To describe the positive contribution, we use a two-band model referring to multiple subbands in Ag-doped ZnO. The conduction band of doped ZnO splits two subbands for spin-up and spin-down carriers.¹⁹⁸ The distribution of these carriers depends on the spin-splitting effect, the thermal activation energy and the temperature. The formula of the magnetic field dependent MR can be obtained by solving the Boltzmann transport equation:^{137,180,199}

$$MR_+ = a^2 H^2 / (1 + b^2 H^2)$$

$$a^2 = \frac{\sigma_1 \sigma_2 (\mu_1 + \mu_2)^2}{(\sigma_1 + \sigma_2)^2}$$

$$b^2 = \frac{(\sigma_1 \mu_2 - \sigma_2 \mu_1)^2}{(\sigma_1 + \sigma_2)^2}$$

where σ_1 , σ_2 and μ_1 , μ_2 represent the conductivity and mobility of carriers corresponding to the subbands.

Figure 3-10 Measured (solid dots) and fitted (solid lines) magnetic field dependence of the MR effect for 2% Ag-doped ZnO bulk sample at different temperature.

Negative MR usually occurs in transition metal doped ZnO in the weak localization regime. It is not suitable for our case. Khosla and Fischer proposed a semiempirical model taking the third-order expansion of the magnetic exchange Hamiltonian into account,²⁰⁰ which can be expressed as^{180,198-200}

$$MR_- = -c^2 \ln(1 + d^2 H^2)$$

$$c^2 = A_1 J D(\epsilon_F) [S(S+1) + \langle M^2 \rangle]$$

$$d^2 = [1 + 4S^2 \pi^2 (\frac{2JD(\epsilon_F)}{g})^4] (\frac{g\mu_B}{\alpha k_B T})^2$$

where A_1 , J , $D(\epsilon_F)$, S , and $\langle M \rangle$ represent the contribution of spin scattering, the

exchange integral, the density of states at the Fermi energy, the spin of the localized magnetic moment and the average magnetization, respectively. g , μ_B , α and k_B represent the effective Landau factor of the localized magnetic moment, the Bohr magneton, the numerical constant and the Boltzmann constant, respectively.

Least-squares fit to the measured MR data is performed based on combining contributions of positive MR and negative MR. In Figure 3-10, the measured data are well fitted by the theoretical model over the whole temperature regime. The fitting parameters show a temperature and concentration dependence. The fitting parameters a and b are responsible for the positive MR, and they decrease with increasing temperature. At high temperature regime, these positive components become neglected, leaving the negative components which dominate the corresponding MR effect. The fitting parameter d decreases linearly with T^{-1} , which is consistent with the proposed theory.

§ 3.5.3 Summary

The MR effect of 2% Ag-doped ZnO bulk ceramic sample is examined via PPMS with temperature range of 5 – 300 K and magnetic field up to 10 T. The MR behavior shows strong temperature dependence. Since the calculation from Hall Effect measurement indicates the sample not weak localized, we applied a semiempirical model combined by the positive contribution and the negative contribution to explain the measured MR data. The positive MR is described by a two-band model, while the negative MR is expressed by the model taking the third-order expansion of the magnetic exchange Hamiltonian into account. Good agreement between the experimental data and the theoretical fitting is obtained for whole temperature range. These results suggest the

magnetic exchange interaction of wide band gap oxides can be rationally tailored by doping different transition elements.

Chapter 4

THz Conductivity of Ag- and Cu-doped ZnO Thin Films

§ 4.1 Introduction

THz time-domain spectroscopy (THz-TDS) based on femtosecond laser techniques has been given considerable attention recently as an invaluable probe to study materials properties, such as the complex refractive index, conductivity, and dielectric response in THz spectral region, which provide particular insight to the fundamentals of charge transport in these materials.^{75,77} The sensitivity of THz-TDS to low frequency vibrations and free charges promises this technique as a good candidate to probe the couplings between those low frequency vibrations and free charges resulting in the polaronic transport. Comparing with conventional transport measurement techniques, THz-TDS can explore the fundamentals of charge transport mechanisms in materials by examining the material response at frequencies high up to those of carrier-scattering processes. In addition, it can overcome the limitations existed in the conventional transport measurements, such as the requirement of good electrical contacts which might induce impurities. Furthermore, THz-TDS measurement can measure the amplitude and phase independently, and thus extracts both the real and imaginary conductivity independently without Kramers-Kronig analysis.⁷⁵ Thanks to these advantages, THz-TDS has been employed to study cooper pairs in superconductors,²⁰¹ bound states in

semiconductors,²⁰² metal-insulator transitions in metal oxides,²⁰³ efficiencies for the formation of excitations and charge carriers in polymers,²⁰⁴ dynamics of liquids and biological molecules,²⁰⁵⁻²⁰⁶ *etc.*

Due to the various optical properties, ZnO based devices were demonstrated to operate in green, blue, red and ultraviolet spectral regions.¹²⁶⁻¹²⁸ Also, great attention has been paid on the THz responses of ZnO based materials these years. Azad *et al.* presented the complex dielectric properties of single-crystal ZnO with high resistivity in the THz regime, and demonstrated the transverse optical E_1 phonon mode dominating the absorption.²⁰⁷ Baxter *et al.* fitted the complex THz conductivity of bulk ZnO by generalized Drude model, allowing a distribution of carrier relaxation times.²⁰⁸ The THz properties of ZnO thin films grown on different substrates have also been described by Drude theory.²⁰⁹⁻²¹⁰ Besides, Baxter *et al.* investigated the conductivity of ZnO in the forms of nanoparticles, nanowires, and thin films using time-resolved THz spectroscopy, and demonstrated the large change of electron lifetime due to the morphology.²¹¹ Moreover, doping different groups of elements into ZnO can induce remarkable properties, as discussed mainly in Chapter 3. For example, Ag-doped ZnO samples became more conductive whereas Cu-doped ZnO samples more insulating compared with the undoped ZnO.^{20,116} These motivate us to investigate the THz complex conductivity of Ag- and Cu-doped ZnO thin films with the purpose to study mechanisms for the polaronic transport.

In this chapter, we present a THz time-domain spectroscopic study of Ag- and Cu- doped ZnO thin films in the temperature range (10 K – 300 K) with a frequency range from 0.3 to 2.8 THz. The complex conductivity are well-described by the

Drude-Smith model, which provide us the temperature dependent carrier lifetime and carrier concentrations.

§ 4.2 Sample Preparation and Characterizations

Ag- and Cu-doped ZnO thin films were deposited on the two-side polished and 1 mm-thick quartz (001) (CrysTec GmbH, Berlin Germany) by PLD with a solid state laser ($\lambda = 355$ nm). A commercial undoped ZnO target was used to prepare the undoped ZnO thin film. For Ag- and Cu-doped ZnO targets with 5% doping concentration, high purity powders were weighed in stoichiometric proportions, mixed in a ball milling, and sintered in air at 1200°C for 24 h with intermittent grinding to enhance the uniformity, as described in Chapter 3. The deposition temperature, time and oxygen pressure of thin films are 450 °C, 1 h and 1 Pa, respectively.

The structural property of undoped, Cu- and Ag-doped ZnO thin films has been examined by using HRXRD (Smartlab, Rigaku Japan). Figure 4-1 displays the θ -2 θ XRD patterns of three samples. Besides the signal of z-cut quartz, there is only (0002) peak observed, indicating highly c-axis orientated with pure phase. The film thickness was measured by SEM, as shown in Figures 4-2 (a), (c) and (e). Cross-sectional view exhibits a sharp edge between thin film and substrate. The thicknesses of undoped, Cu- and Ag-doped ZnO thin films are round 346 nm, 206 nm and 125 nm, respectively. AFM topography images [see Figures 4-2 (b), (d) and (f)] show a uniform morphology for all three samples, with fine roughness of ~ 4.0 nm, 0.2 nm and 0.3 nm, respectively.

Figure 4-1 Typical XRD patterns of Cu- and Ag-doped ZnO thin films grown on z-cut quartz, with undoped ZnO thin film as reference.

Figure 4-2 SEM images (cross-section view) and AFM images for undoped, Ag- and Cu-doped ZnO thin films.

§ 4.3 Experimental Details and Data Acquisition

The investigation of THz properties was performed by a commercial THz–TDS system (TeraView Spectra 3000), where the THz wave was generated and detected by photoconductive antennas fabricated on low-temperature-grown GaAs films. The sample (undoped, Cu- or Ag-doped ZnO thin films) was attached to a copper holder and centered over a 7-mm-diameter hole in the plate, which defines the optical aperture. Another piece of z-cut quartz went through the same heat treatment and was used as a reference attaching to the other identical clear hole. For each sample or reference run, 900 THz scans were collected over 180 seconds. The whole experiment was taken in a closed chamber purged with dry air to reduce THz absorption by water vapor. A continuous flow Helium-4 cryostat, with an attached motorized linear stage was applied to examine the temperature dependence of THz properties ranging from 10 to 300 K.

For data acquisition, we take the undoped ZnO thin film as an example. The transmitted electric field of THz pulses through the undoped ZnO sample and the z-cut quartz reference are recorded in the time domain, as shown in Figure 4-3(a). The peak intensity of the main transmitted THz pulse through the undoped ZnO sample is slightly smaller than that of the reference THz pulse through the z-cut quartz, indicating a small absorption of THz pulse. The data analysis focuses on the main transmitted THz pulse because of the distinct separation between the main THz pulse and the etalon contributed by multiple reflections. Figure 4-3(b) displays the corresponding spectra of amplitude and phase after applying FFT.

Figure 4-3 (a) Time-domain THz pulse transmitted through the undoped ZnO sample and z-cut quartz reference at temperature of 10 K. (b) Amplitude spectra in frequency domain after applying FFT.

Since the absorption of the THz pulse by undoped, Cu- and Ag-doped ZnO thin films is small, we must examine the confidence intervals for this measurement. As suggested in Chapter 2, the experimental transmission coefficient (or transmittance) was defined as $\tilde{T}(\omega) = \tilde{E}_s(\omega)/\tilde{E}_r(\omega)$, where $\tilde{E}_s(\omega)$ and $\tilde{E}_r(\omega)$ are the frequency-dependent transmitted electric field of THz pulse through sample and reference, respectively. Firstly we performed the transmission coefficient when both of sample and reference are vacuum. As shown in Figure 4-4, the solid line representing the amplitude of transmittance was obtained, suggesting less than 0.5% of deviation from the ideal value of 1. After that, the amplitudes of transmittance for undoped, Cu- and Ag-doped ZnO thin films were also depicted in Figure 4-4. From the comparison in this figure, we can conclude that there

was almost no absorption of THz pulse for the Cu-doped ZnO thin film, while that for the undoped ZnO thin film was the largest. These results were consistent with our previous electrical properties, where the Cu-doped ZnO showed much higher resistivity compared to the undoped ZnO sample. Thus, for further analysis, we mainly focused on the undoped and Ag-doped ZnO thin film samples.

Figure 4-4 Amplitude of transmittance for undoped, Cu- and Ag-doped ZnO thin films at 10 K. The solid line represents the transmittance amplitude with both sample and reference referred to vacuum. The vertical dashed lines give the frequency window for further data analysis.

Theoretically, $\tilde{T}(\omega)$ can be expressed as:¹⁰²

$$\tilde{T}(\omega) = \frac{\tilde{E}_s(\omega)}{\tilde{E}_r(\omega)} = \frac{2\tilde{n}(\tilde{n}_{sub} + 1)\exp[i\omega d(\tilde{n} - 1)/c]\exp[i\omega \Delta L(1 - \tilde{n}_{sub})/c]}{(1 + \tilde{n})(\tilde{n} + \tilde{n}_{sub}) + (\tilde{n} - 1)(\tilde{n}_{sub} - \tilde{n})\exp[2i\omega d\tilde{n}/c]}$$

where $\tilde{n}$ and $\tilde{n}_{sub}$ refers to the complex refractive indices of undoped/Ag-doped ZnO sample and z-cut quartz substrate, respectively. d refers to the thickness of the measured

sample, ΔL refers to the thickness difference between sample and reference substrates (when the reference substrate is thinner the sample substrat, ΔL is negative), c refers to the speed of light in vacuum. The complex refractive index of z-cut quartz was measured with the same method mentioned in Chapter 2. Figure 4-5 displays the refractive index (n) and extinction coefficient (k) of z-cut quartz versus the THz frequency at various temperatures. The temperature independence, the THz frequency independence, and the very small extinction coefficient (which means the z-cut quartz is almost transparent to THz radiation) make z-cut quartz as a good choice of substrate used in the THz investigation. In this data acquisition, the average value of refractive index $n \sim 2.10$ and

Figure 4-5 The refractive index (a) and extinction coefficient (b) of z-cut quartz with temperature range 10 – 300 K.

the extinction coefficient $k \sim 0.002$ were used. From the formula of the complex transmittance, we can apply the numerical iteration to obtain the complex refractive index of investigated thin film sample, $\tilde{n}(\omega) = n(\omega) + ik(\omega)$. Then the complex conductivity can be calculated as $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$, where $\sigma_1(\omega) = 2\varepsilon_0 n(\omega)k(\omega)$, and $\sigma_2(\omega) = \omega\varepsilon_0[\varepsilon_\infty - n^2(\omega) + k^2(\omega)]$. Here, ε_∞ is the high frequency dielectric constant, and ε_0 is the free space permittivity of the investigated thin film sample ($\varepsilon_\infty = 3.705$ for ZnO^{212}). The complex dielectric function can be calculated as $\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega)$, and $\varepsilon_2(\omega) = 2n(\omega)k(\omega)$.

§ 4.4 Conductivity Models and Result Discussions

The complex refractive indices of undoped and Ag-doped ZnO thin films are plotted in Figure 4-6. The refractive index of undoped ZnO thin film decreases with increasing frequency. Similar phenomena have been obtained in *n*-type polycrystalline ZnO thin film and nanostructures,²¹¹ *n*-type single-crystal ZnO epilayer²¹⁰ and *n*-type GaN epilayer.²¹³ By comparing both of the refractive index and absorption coefficient between 10 K and 300 K, we find that they increase with increasing temperature. Zhang *et al.* studied the THz responses of *n*-type single-crystal ZnO thin film with different carrier concentration, and suggested that higher free carrier concentration can result in high refractive index and absorption coefficient.²¹⁰ This is consistent with our results from the fitting of complex conductivity, which will be discussed later. After doping with Ag element, both of refractive index and absorption coefficient are smaller comparing with those of the undoped ZnO sample, and almost frequency independent for the whole THz frequency region. Besides, there is no obvious temperature dependence in the Ag-doped ZnO thin

film. The complex dielectric functions of undoped and Ag-doped ZnO thin films are shown in Figure 4-7.

Figure 4-6 Complex refractive indices of the undoped and Ag-doped ZnO thin films at temperature of 10 K and 300 K, respectively.

Figure 4-7 Complex dielectric functions of the undoped and Ag-doped ZnO thin films at temperature of 10 K and 300 K, respectively.

Figure 4-8 displays the complex conductivity of undoped and Ag-doped ZnO thin films at temperature of 10 K. The real conductivities of both samples show a small conductivity, with that of the undoped ZnO sample slightly higher than the Ag-doped ZnO sample. Previous reports suggested the properties of ZnO based thin films could be largely modified by the deposition condition and post annealing.¹⁰⁹ Normally, defects can be easily induced when ZnO thin films grown in the vacuum, which contributes to high carrier concentration and therefore the conductive behavior exhibits. Our undoped and Ag-doped ZnO samples were synthesized at high oxygen pressure, which avoids the situation of oxygen defects and results in a poor conductivity typically for semiconductors. The imaginary conductivities are negative, and decreases with increasing frequency. Such complex conductivity spectra of our samples fundamentally differs from the typical characteristics for a conductive or non-conductive-type response, and similar to the previous reports.^{202,214-217}

Before the further discussion on the complex conductivity, we introduce several related theoretical conductivity models: Drude model, Drude-Smith model, Lorentz model and Drude-Lorentz model. Proposed by Paul Drude in 1900, Drude model is the most simplest and well-known conductivity model.²¹⁸ Carriers are considered free and independent in this model, and their motion depends on the direction which carriers travel in and the thermal equilibrium. When an electric field is applied, carriers move slightly along a certain direction, resulting in a net drift velocity. By solving this drift velocity in Newton's laws, the complex Drude conductivity formula can be written as²¹⁹

$$\tilde{\sigma}(\omega) = \frac{Ne^2\tau/m^*}{(1 - i\omega\tau)}$$

where N , e , τ and m^* represent the carrier density, electron charge, relaxation time and effective mass, respectively. Normally, the real conductivity decreases with increasing frequency with its maximum value at zero frequency, while the imaginary conductivity is positive with its maximum value at the frequency of carrier scattering rate. The Drude model has been used to describe the complex conductivity of various material systems, such as sapphire,²²⁰ rutile TiO₂,²²¹ nanoporous InPa,²²² doped silicon,⁷⁸ GaN²¹³ and other semiconductors.

In some material systems including nanomaterials and poor metals, Drude model can not well describe their conductivity behavior. For example, the real conductivity has a non-zero frequency maximum, and the imaginary conductivity becomes negative. Negative imaginary conductivity can be resulted from the backscattering of electrons after collisions,²⁰² the effective medium theory²¹⁷ and the polarizability of excitons.²²³ Thus, Smith proposed a new modification,²²⁴⁻²²⁵ named as Drude-Smith model, and the formula can be written as

$$\tilde{\sigma}(\omega) = \frac{Ne^2\tau/m^*}{(1 - i\omega\tau)} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega\tau)^n} \right]$$

This formula is usually truncated by leaving the first scattering event only, and c_1 represents the cosine value of the scattering angle. c_1 changes from -1 to 0 , depending on the backscattering or localization. This model leads to a negative imaginary conductivity and suppresses the real conductivity near zero frequency. $c_1 = -1$ means the complete carrier backscattering or localization, while $c_1 = 0$ returns to normal Drude model. The Drude-Smith model has been often used to describe the complex conductivity of material systems with significant carrier localization, where $c_1 \approx -1$, such as

dye-sensitized solar cells,²⁰² nanocrystalline silicon²¹⁶ and ZnO nanoparticles.²¹¹ Although this model was criticized being unphysical,²²⁶⁻²²⁸ its utility has become more often. Monte Carlo simulations of carrier scattering demonstrate Drude-Smith model-like frequency dependence, which suggests a relation between fitting parameters and physical processes that result in carrier localization.²²⁹

The Lorentz model is usually employed to describe the resonant feature of spectra caused by various origins. The formula can be expressed as²¹⁹

$$\tilde{\sigma}(\omega) = \sum_j \frac{\omega_{pj}^2 \varepsilon_0 \omega}{i(\omega_{0j}^2 - \omega^2) + \gamma_j \omega}$$

where ω_{pj} , ω_{0j} and γ_j are oscillator strength, resonance frequency and oscillator damping constant (spectral width) respectively of the j -th Lorentz resonance mode. The Lorentz oscillator peaks at the resonant frequency. When the frequency is below the resonance frequency, the real conductivity increases with increasing frequency, and the imaginary conductivity is negative. Actually, Drude-Lorentz model is more often considered to describe the conductivity, with formula expressed as²³⁰⁻²³¹

$$\tilde{\sigma}(\omega) = \frac{\varepsilon_0 \omega_p^2}{(\gamma - i\omega)} + \sum_j \frac{\omega_{pj}^2 \varepsilon_0 \omega}{i(\omega_{0j}^2 - \omega^2) + \gamma_j \omega}$$

This model has been often used to describe the material systems including excitons in GaAs,²³² bound polarons in organic heterojunction solar cells,²³³ plasmon resonances of isolated silicon particles,²¹⁵ and so on.

The non-zero frequency maximum for the real conductivity as well as the negative imaginary conductivity motivate us to employ the Drude-Smith model for the theoretical fitting of complex conductivity in undoped and Ag-doped ZnO thin films. Good agreement between the measured conductivity and the theoretical fitting is obtained, as

Figure 4-8 Complex conductivity of undoped and Ag-doped ZnO. Solid lines represent the theoretical fitting results by applying the Drude-Smith model.

shown in Figure 4-8. The electron effective mass $m^* = 0.24 m_e$ is used for ZnO.²³⁴ The fitting parameter c_1 is around -0.9 for both samples at various temperatures, which is similar to the case of Anderson localization ($c_1 = -1$).²³⁵ Another fitting parameters, carrier density and relaxation time, are plotted versus temperature, seeing Figure 4-9. The carrier density of the undoped ZnO thin film is on the order of 10^{19} cm^{-3} , similar to the previous report.^{209,236} The increase of carrier density with increasing temperature is consistent with our results of complex refractive index. For the Ag-doped ZnO thin film, the almost temperature independent carrier density is lower than that of undoped sample, leading to a poorer real conductivity. As the temperature increases, the relaxation time of the undoped ZnO thin film decreases, while that of the Ag-doped sample has no obvious dependence of temperature. These results suggest the carrier localization in our samples,

especially the Ag-doped ZnO thin film. Further theoretical simulations are needed to confirm the relation between the fitting results and the carrier localization.

Figure 4-9 The fitting parameters (carrier density and relaxation time) of the undoped and Ag-doped ZnO thin films. They are extracted from the Drude-Smith model and plotted as a function of temperature.

§ 4.5 Summary

The THz conductivity of undoped, Cu- and Ag-doped ZnO thin films grown on the z-cut quartz substrate have been investigated by THz-TDS at different temperatures. There is no absorption of THz pulse for Cu-doped ZnO thin film, suggesting the sample is highly insulating and transparent of THz radiation. The measured complex conductivities of undoped and Ag-doped ZnO thin films are well fitted by the Drude-Smith model. The extracted carrier density increases and relaxation time decreases with increasing temperature for the undoped ZnO thin film, while that for the Ag-doped ZnO thin film has no obvious dependence of temperature. These results suggest our samples are in the localized regime.

Chapter 5 THz–TDS of BiFeO₃ Thin Films Grown on SrLaAlO₄

Recently, multiferroics has attracted considerable interest due to the exciting multiferroic properties which promise the great potential applications. BiFeO₃ (BFO) is a promising candidate due to its robust ferroelectric and magnetic properties. Here we investigate the THz response of the BFO thin film grown on the SrLaAlO₄ (SLAO) substrate by employing the unique THz–TDS. Firstly, we conducted the THz characterization of the as-grown and annealed SLAO substrates. Their complex dielectric responses are well described by the Lorentz model. The free carriers were reduced in the SLAO substrate by the thermal annealing. This result suggests the SLAO a good candidate of substrates used to study the THz properties in thin film system. The extracted complex refractive indices were used in the investigation of the BFO thin film. Finally the THz responses of the BFO thin film were discussed.

§ 5.1 THz Dielectric Properties of SLAO substrate

In this section, the far-infrared dielectric properties of SLAO single crystal is studied by THz–TDS with different temperatures (10 K – 300 K) over a frequency range of 0.4 – 2.6 THz. Drude-Lorentz model with two resonance modes well describe the complex dielectric response. Thermal annealing leads a great reduction of free charge carriers in the substrate, removing the Drude contribution, leaving only the Lorentz term. This study provides an important contribution to the characterization of SLAO substrates which are always used in the synthesis of functional thin films.

§ 5.1.1 Introduction to SLAO

Frequency-dependent complex conductivity and dielectric response are basic properties of materials and essential for device applications. THz-TDS is a powerful technique to examine such properties in the THz spectral region, with advantages of no requirement for Kramer-Kronig transformation, noncontact optical probe and high signal-to-noise ratio.^{72,237} The knowledge of substrate materials at THz frequency, which are commonly used in the synthesis of high-temperature superconducting and other functional thin films, is important in the understanding the development of technological devices.^{207,238-239} As a well-known substrate, SLAO is a tetragonal crystal with K_2NiF_4 structure, belonging to the space group $I4/mmm$.²⁴⁰ The aluminum atoms with each surrounded by six oxygen atoms occupy D_{4h} sites, thus forming AlO_6 layers in the ab plane. Sr and La ions are between the layers and distributed randomly in nine-coordinated sites of C_{4v} symmetry. High dielectric constant and very low dielectric loss in the microwave frequency region promise SLAO to be an excellent material for microwave dielectric applications.²⁴¹ Fan *et al.* demonstrated the intrinsic dielectric properties of SLAO ceramics at microwave frequencies.²⁴² Besides, optical spectroscopy studies have been conducted on single crystals of pure SLAO, SLAO doped with rare earth ions (e.g. Nd^{3+} , Pr^{3+}) and transition ions (e.g. Cr^{3+}), which were aimed towards an understanding of lasing behavior.²⁴³⁻²⁴⁴

Recently, much attention has been paid on THz properties of complex oxide thin films. SLAO is a suitable substrate for growth of perovskite thin film because of the identical structure along the ab plane.²⁴⁵ Besides, the advantage of SLAO in THz region is

obvious comparing with the similar structure with compositions such as LaAlO_3 or SrTiO_3 , as LaAlO_3 is usually heavily twinned and SrTiO_3 has high dielectric loss in this region. There are different order parameters (e.g. charge, spin, lattice) in such strongly correlated electron systems, and the coupling or completing among these parameters is crucial for the material properties. Low-energy dynamics, particularly at THz frequencies, could frequently reveal the interplay among these parameters.²⁴⁶ However, the extraction and analysis of THz data critically depend on the relative parameters of the underlying substrate. So far the THz frequency parameters of SLAO single crystal have not been reported in detail. Moreover, the effect of annealing on optical properties of annealed SLAO should be considered, because most thin film synthesis requires high temperatures which unavoidably involve the annealing of the substrates as well.

Here, with a frequency range from 0.4 to 2.6 THz, the temperature-dependent (10 K – 300 K) complex dielectric response of as-grown and annealed SLAO single crystals were experimentally characterized by use of THz–TDS. The complex dielectric constant $\tilde{\epsilon}$ are well-described by the Drude-Lorentz model for the as-grown substrate. Moreover, when the substrate is annealed and re-measured, the free charge carriers were greatly reduced, eliminating the Drude contribution and leaving only the Lorentz term with two oscillators.

§ 5.1.2 Experimental Details and Data Acquisition

The SLAO (100) substrate is a 5 mm $\times$ 5 mm $\times$ 1 mm-thick single crystal grown using the Czochraski method, with both sides optically polished (CrysTec GmbH, Berlin Germany). A commercial THz–TDS system (TeraView Spectra 3000) was used here to examine the THz dielectric response of the SLAO substrate. The SLAO substrate was

placed on a cooper holder and measured by using vacuum as a reference. The detailed measurement was described in Chapter 2.

Figure 5-1 (a) Time-domain THz pulses transmitted through the SLAO substrate and air reference. (b) Amplitude spectra in frequency domain after applying FFT. The inset shows the frequency dependent phase spectra.

The transmitted electric field of THz pulses through the SLAO substrate and the reference are recorded in the time domain, as presented in Figure 5-1(a). The peak of the main transmitted THz pulse through the SLAO substrate decreases in intensity due to absorption, and delayed, when compared with that of the reference THz pulse through vacuum. The data analysis is conducted on the main transmitted THz pulse because of the distinct separation between the main THz pulse and the etalon contributed by multiple reflections. Figure 5-1(b) displays the corresponding amplitude and phase spectra after applying FFT. From the frequency-dependent transmitted electric field of THz pulse

through the SLAO sample ($\tilde{E}_s(\omega)$) and reference ($\tilde{E}_r(\omega)$), the complex transmission coefficient $\tilde{T}(\omega)$ can be derived to be

$$\tilde{T}(\omega) = \frac{\tilde{E}_s(\omega)}{\tilde{E}_r(\omega)} = \frac{4\tilde{n}(\omega)}{(1 + \tilde{n}(\omega))^2} \exp [i\omega d(\tilde{n}(\omega) - 1)/c]$$

where d and $\tilde{n}(\omega)$ are the thickness and complex refractive index of the SLAO substrate respectively, and c is the speed of light in vacuum. The complex refractive index $\tilde{n}(\omega)$ can be obtained by numerically solving the equation above. The complex dielectric response $\tilde{\epsilon}(\omega)$ can be obtained via the relationships:

$$\tilde{n}(\omega) = n(\omega) + ik(\omega)$$

$$\tilde{\epsilon}(\omega) \equiv \epsilon_1(\omega) + i\epsilon_2(\omega) = [\tilde{n}(\omega)]^2$$

§ 5.1.3 Results and Discussions

The experimentally extracted refractive indices $\tilde{n}(\omega)$ of as-grown SLAO substrate are presented in Figure 5-2, with the frequency region of 0.4 – 2.6 THz. Figure 5-2(a) shows that the real part of refractive index $n(\omega)$ grows with increasing frequency, with slightly temperature dependent, which is similar to the behavior of LaAlO_3 .²⁴⁷ The extinction coefficient $k(\omega)$ is very small and nearly frequency independent between 0.6 – 2.0 THz shown in Figure 5-2(b). At low frequencies, $k(\omega)$ increases with decreasing frequency, possibly because of the presence of free charge carriers. The refractive index results represented in Figure 5-2 suggest that the as-grown SLAO has a phonon mode near the experimental frequencies, which can be shown in the following analysis of complex dielectric response.

Figure 5-2 (a) Real and (b) imaginary parts of refractive index of the as-grown SLAO substrate as a function of frequency with different temperatures.

Figure 5-3 represents the frequency-dependent complex dielectric response. Generally the far-infrared THz absorption of crystals could be induced by the interactions between a radiation field and fundamental phonons as a result of creation or annihilation of lattice vibrations. Moreover, as discussed before, there were free charge carriers which dominated at low frequencies. So we employ a model to describe the complex dielectric response, which combines a Drude term and localized Lorentzian absorptions, as expressed

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}$$

where $\epsilon_{\infty} = 4.2$ is the high frequency dielectric constant for SLAO.²⁴² The first and

second terms are from Drude model which describes the free carrier dynamics in a good metal, and the parameter ω_p refers to plasma frequency while γ is the relaxation rate of charge carriers. From ω_p and γ , the free carrier concentration can be obtained via $N = \omega_p^2 m^* \epsilon_0 / e^2$, and the dc mobility obtained via $\mu = e / \gamma m^*$, where m^* is the electron effective mass. The third term represents the Lorentz harmonic oscillators, where ω_{pj} , ω_j and Γ_j are oscillator strength, resonance frequency and spectral width respectively of the j -th Lorentz resonance mode. The experimental data (solid symbols) was well verified by the model (solid lines), as shown in Figure 5-3.

Figure 5-3 Real and imaginary parts of complex dielectric response of the as-grown SLAO substrate as function of frequency, where the solid lines are fitting results.

By fitting the complex dielectric response based the Drude-Lorentz model, two resonance modes were used, with parameters (taking the data at 10 K as an example)

listed in Table 5-1. A previous report studied the intrinsic microwave dielectric properties of SLAO ceramics and extracted a polar-phonon mode with frequency 215 cm^{-1} , which came from the bending and stretching vibrations of $(\text{Sr, La})\text{-AlO}_6$,²⁴² and this is consistent with our first resonance mode (6.57 THz). Our second resonance mode with frequency centered 3.05 THz is smaller than the reported 3.6 THz, which was obtained by investigating the dielectric properties of LaAlO_3 at THz frequencies.²⁴⁸ In the standard quasiharmonic model (QH), the relation between the rates of change in volume of a crystal and softening of the average phonon energy can be expressed as: $\Delta\langle E\rangle/\langle E\rangle = -\bar{\gamma}\Delta V/V$, where $\bar{\gamma}$ is an average Gruneisen parameter and usually positive.²⁴⁹ The increased volume in the as-grown SLAO substrate comparing with LAO was due to the larger effective ionic radius of Sr^{2+} (1.31 Å) than that of La^{3+} (1.216 Å).²⁴² Therefore it leads to the smaller value of resonance frequency.

Table 5-1 Parameters obtained by fitting the experimental complex dielectric response of the as-grown and annealed SLAO substrate at 10 K.

SLAO	ω_{p1} (THz)	ω_1 (THz)	Γ_1 (THz)	ω_{p2} (THz)	ω_2 (THz)	Γ_2 (THz)
As grown	23.13±0.055	6.57±0.02	0.031±0.005	1.15±0.09	3.05±0.04	0.432±0.016
Annealed	23.02±0.05	6.59±0.02	0.007±0.006	1.44±0.10	3.16±0.04	0.477±0.014

Figure 5-4 The comparison of complex dielectric response for the SLAO substrate before and after annealing, where the solid lines are fitting results.

With the purpose of investigating the effect of annealing on the optical properties of the SLAO substrate, the as-grown SLAO substrate was annealed in a furnace at 700 °C for 2 hours, with high oxygen pressure. THz–TDS data were taken in this annealed SLAO substrate, with the THz complex dielectric response shown in Figure 5-4. Compared to the as-grown data, we see a difference in the low frequency behavior, where ϵ_2 is now close to zero and almost frequency-independent. Annealing with high oxygen pressure presumably makes the lattice of SLAO substrate more stoichiometric by eliminating ionized oxygen vacancies and interstitials, thus reducing the concentration of free charge carriers. Hence the Drude term sets suppressed, yielding a pure Lorentzian contribution to

$\varepsilon(\omega)$:

$$\tilde{\varepsilon}(\omega) = \varepsilon_{\infty} + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}$$

Table 5-1 lists the fitting parameters (taking the data at 10 K as an example). From this Table, the resonance frequencies obtained by fitting the dielectric response of annealed SLAO slightly larger than that of as-grown SLAO, which can also be ascribed to the standard QH model. After annealing, the elimination of ionized oxygen vacancies and interstitials not only suppressed the Drude term, but also increased the crystallinity of the SLAO substrate. Such effect caused the decrease of volume slightly, leading to a slightly larger value of resonance frequency. In Figure 5-5, the fitting parameters of as-grown SLAO and annealed SLAO appears as a function of temperature, where the Γ values increase with increasing temperature.

Figure 5-5 Comparison of fitting parameters between as-grown SLAO and annealed SLAO as a function of temperature, where the black symbol is for as-grown SLAO and the red symbol is for annealed SLAO.

§ 5.1.4 Summary

In conclusion, the THz frequency-dependent complex dielectric responses of as-grown and annealed SLAO single crystals are characterized by THz-TDS.

Drude-Lorentz model well describes the complex dielectric constant for the as-grown SLAO. As the free charge carriers are reduced, the complex dielectric constant of annealed SLAO can be fitted only by Lorentz terms with two oscillators. Our results provide important information for THz study on the thin film systems synthesized on the SLAO substrate.

§ 5.2 THz Properties of BFO Thin Films

§ 5.2.1 Introduction to BFO Thin Films

Multiferroic materials have multiple degrees of freedom and thus offer an intriguing fundamental physics which shed light on the wide range of potential applications.^{32,37} As one of the most investigated multiferroic materials, BFO has a single phase and possesses simultaneous ferroelectric order with a large polarization ($\sim 100 \mu\text{C}/\text{cm}^2$), and magnetic order with high Curie temperature ($\sim 1100 \text{ K}$) at room temperature. Bulk BFO has a rhombohedrally distorted perovskite structure with space group $R3c$,²⁵⁰ and lattice parameters are $a_{\text{rh}} = 3.965 \text{ \AA}$ and $\alpha_{\text{rh}} = 89.4^\circ$.³⁵ A ferroelectric polarization along [111] can be obtained in bulk BFO, due to the displacement of the Bi^{3+} and Fe^{3+} cations along the [111] threefold polar axis as well as the off-center to the barycenter of the oxygen polyhedral.³⁶ On another side, the Fe^{3+} magnetic moments are aligned ferromagnetically in (111) planes but antiferromagnetically between adjacent planes. So the weak ferromagnetism is resulted from the canting of antiferromagnetic sublattices with magnetic moments perpendicular to the [111] direction. Such robust ferroelectricity, multiferroic properties and lead-free nature make BFO an excellent candidate for next generation devices.

Spectroscopic studies on lattice and magnetic excitations are employed to investigate its magnetism and ferroelectricity, as well as their coupling effect.^{41,251} BFO has a charge gap of 2.67 eV at 300 K ascribed to the charge transfer from the O 2*p* to Fe 3*d*.^{39,252-253} The spin-phonon coupling in single crystal BFO and epitaxial BFO thin films has been demonstrated by Raman studies. Raman spectra with phonon mode in BFO thin films was first discussed by Singh *et al.*²⁵⁴ All 13 Raman modes were examined in polycrystalline and single crystal BFO by Kothari *et al.*²⁵⁵ and Fukumura *et al.*,²⁵⁶ respectively. Moreover, magnetodielectric effect and polar phonons in BFO ceramics were examined in the infrared and THz regime by Kamba *et al.*⁴¹ Talbayev *et al.* performed a THz study of the single crystal BFO and reported the out-of-plane resonance modes would split due to the modulated Dzyaloshinski-Moriya interaction.⁴² These optical investigations on BFO with various morphologies would help us to unravel the detailed mechanisms of magnetism and ferroelectricity, as well as their coupling effect.

The properties of BFO can be modified by the technique of thin-film growth.^{107,250,257-258} Ramesh *et al.* reported the change of crystal symmetry in the BFO thin film grown on the SrTiO₃ (STO) substrate, due to their lattice mismatch.³⁷ Wu *et al.* found the occurrence of orbital reconstructions between BFO and La_{0.7}Sr_{0.3}MnO₃ thin films, due to their interface effect between this heterostructures.³⁸ Here the THz response of the BFO thin film grown on SLAO by using commercial THz–TDS was studied, with the purpose of addressing the origins of magnetism and ferroelectricity in the BFO thin film. Also effects of SLAO substrate would be considered.

§ 5.2.2 Sample Preparation and Characterizations

PLD with a pulsed KrF excimer laser ($\lambda = 248\text{ nm}$) was used to grow BFO thin films on the (001) SLAO single crystal substrate at a repetition rate of 5 Hz. The deposition was conducted at 700 °C at 10 Pa oxygen pressure. After that, the films cooled down to room temperature with 5 °C/min and 1 atm oxygen pressure. Bi₂O₃ precipitates at the lower temperature or higher pressure, while Fe₂O₃ forms at the lower pressure or higher temperature.²⁵⁹

In Figure 5-6(a), high resolution XRD spectra demonstrated the crystallinity and crystal orientation of the BFO thin film. Only 00 l type diffraction peaks were observed. Calculated from the high angle peak position, the out-of-plane lattice parameter is 4.66 Å, much larger than 3.96 Å which is for bulk BFO, suggesting the film is close to tetragonal-like (T) phase with large misfit strain. This result agrees with previous theoretical and experimental reports.²⁶⁰⁻²⁶² The characteristic topographic and piezoresponse phase images were performed by AFM (Asylum Research, USA, MFP-3D). In Figure 5-6(b), the topographic image demonstrates the uniform surface with two distinct features, and its root mean square roughness (R_{rms}) is $\sim 1.47\text{ nm}$. The T phase results to plateau feature while stripe-like feature comes from T and rhombohedral-like (R) multiphase.²⁶¹ The in-plane PFM image [see Figure 5-6(c)] shows a regular domain structure, which is similar to that in BFO thin films on STO but with a different orientation.²⁶³ That indicates the polarization vector probably titles a certain angles comparing to that of BFO thin films on STO. The out-plane PFM image illustrates a uniform contrast in Figure 5-6(d), implying all out-of-plane polarizations point in one direction.²⁶¹

Figure 5-6 (a) High resolution XRD θ - 2θ scans of BFO thin film grown on the SLAO substrate. The blue symbols represent XRD peaks from the SLAO substrate. (b) Topographic AFM image. (c) In-plane PFM image. (d) Out-of-plane PFM image.

§ 5.2.3 Experimental Details and Data Acquisition

The investigation of the BFO thin film grown on SLAO in THz regime was performed by a commercial THz-TDS system (TeraView Spectra 3000). Similar to the description in Chapter 4, The BFO thin film sample was placed on a copper holder with a 3.5-mm-diameter hole in the center, and the annealed SLAO was used as a reference. The details during this measurement were mainly discussed in Chapter 2.

The transmitted electric field of THz pulses through the BFO thin film sample and the annealed SLAO reference are recorded in the time domain, as indicated in Figure 5-7(a). The peak intensity of the main transmitted THz pulse through the BFO thin film

sample is slightly smaller than that through the annealed SLAO, indicating a small absorption of THz pulse. The analysis is conducted on the main transmitted THz pulse, and after applying FFT the corresponding amplitude and phase spectra are obtained, as displayed in Figure 5-6(b).

Figure 5-7 (a) Time-domain THz pulse transmitted through the BFO thin film sample and annealed SLAO reference at temperature of 10 K. (b) Amplitude spectra in frequency domain after applying FFT.

Due to the small absorption (see Figure 5-7) of THz pulse by the BFO thin film, we performed the examination of the confidence intervals before the further data analysis, based on the process mentioned in Chapter 4. Figure 5-8 shows the experimental transmittance amplitude as a function of frequency at temperature 10 K and 300 K. In Figure 5-8, the transmission coefficient was examined when both of sample and reference are vacuum, with its amplitude in the black solid line. Less than 0.8% of deviation from

the ideal value of 1 was obtained. By comparing with the transmittance amplitude of vacuum, we found that the absorption by the BFO thin film was very small at low frequency region and increased at high frequency region. So for the further data analysis, we must take care of that at low frequency region, or thicker BFO thin films would be suggested. Here, we mainly analyzed the THz properties of the BFO thin film with frequency ranging from 0.5 – 2.3 THz, followed the same data acquisition process which was discussed in Chapter 4.

Figure 5-8 Amplitude of transmittance for BFO thin film at 10 K and 300 K. The black solid line represents the transmittance amplitude when both sample and reference are vacuum. The vertical dashed lines give the frequency window for further data analysis.

§ 5.2.4 Results and Discussions

Figure 5-9 shows the complex refractive indices of the BFO thin film on SLAO at

different temperatures. With temperature increasing, the refractive index n decreases while the absorption coefficient k increases. The eigenfrequency of 63.3 cm^{-1} well observed especially at low temperature is considered as the infrared E(1) mode, which is consistent to previous report of 64.1 cm^{-1} .²⁶⁴ Kamba *et al.* listed all 13 phonon modes of BFO ceramics by the Raman study, and found the partial softening leads the lowest optical phonon mode from 76 cm^{-1} at 20 K to 67 cm^{-1} at 900 K.⁴¹ Such temperature dependence can be observed for the infrared E(1) mode. Below the lowest phonon mode, there are several modes observed at the eigenfrequencies of 19.5 cm^{-1} , 27.6 cm^{-1} , and 50.6 cm^{-1} , respectively. Singh *et al.* demonstrated two magnon modes in epitaxial BFO thin films, with frequencies of 18.9 cm^{-1} and 27.9 cm^{-1} , respectively,²⁶⁵ which suggested the observed two magnon modes in our sample. The intense peak at 50.6 cm^{-1} always exists in the whole temperature range. Talbayev *et al.* performed the low THz frequency spectroscopic study in bulk BFO crystal, and observed several long-wavelength magnetic resonance modes determined by the magnetic-dipole selection rules.⁴² Komandin *et al.* also found these distinct magnetic resonance modes within $10 - 30\text{ cm}^{-1}$, and besides they revealed an additional absorption lining in the $30 - 60\text{ cm}^{-1}$ with a considerable dielectric contribution.²⁶⁶ They ascribe the corresponding oscillator to the coupling between the magnetic subsystem and lowest frequency phonon mode. That may also explain the observed resonance mode at 50.6 cm^{-1} .

It is important to study the complex conductivity of multiferroic materials, because the dielectric and polarization probing may mislead when polarizability and ac conductivity co-exist in these materials.²⁶⁷ The extracted complex conductivity of the BFO thin film on SLAO at different temperatures is presented in Figure 5-10. The

Figure 5-9 Complex refractive indices of the BFO thin film grown on the SLAO substrate at various temperatures.

Figure 5-10 Complex conductivity of the BFO thin film grown on the SLAO substrate at various temperatures.

high-frequency dielectric constant $\epsilon_{\infty} = 4.0$ was used for BFO.⁴¹ The obtained real conductivity for our BFO sample was on the order around $10^4 \Omega^{-1} \text{m}^{-1}$, much larger than that observed for BFO nanoparticles or polycrystalline BFO in kHz frequency regime.²⁶⁸⁻²⁶⁹ The domains in the BFO thin film (see Figure 5-6(c)) offer the possibility for the high value of conductivity. Seidel *et al.* demonstrated the enhanced conductivity in BFO nanomaterials was related to the electrostatic potential and local electronic structure resulting in the decrease of the band gap at those domain walls.²⁷⁰ Besides, both real and imaginary conductivities increase when frequency increases. The observed intense peak at

50.6 cm⁻¹ still exist in the whole temperature range. Further THz experiments on thicker BFO thin films and theoretical analysis will be conducted.

§ 5.2.5 Summary

The THz responses of the BFO thin film on SLAO were investigated by using THz-TDS. The infrared E(1) mode was observed and the magnon modes at low THz frequency region were discussed. An intense peak at frequency of 50.6 cm⁻¹ may related to the electromagnon excitation. The enhanced conductivity could be ascribed to the domains in the BFO thin film. As the difference between the THz signals through BFO sample and SLAO reference is small, we will grow thicker BFO thin films for further investigations.

Chapter 6 Measuring the Magnetoelectric Coupling in BFO Thin Films by Utilizing Low-Temperature Grown GaAs-based Auston Switch – Preliminary Work

§ 6.1 Introduction

The multiple order parameters in multiferroic materials can offer an exciting coupling between electronic and magnetic ordering. Magnetoelectric (ME) effect describes a phenomenon that a dielectric (magnetic) polarization can be modified by an external magnetic (electric) field.^{31-32,37} Recent reports have demonstrated the switching of magnetization by applying an electric field, opening the potential applications in spintronics, data storage and switching devices.²⁷¹⁻²⁷³ BFO exhibits multiferroic properties with coexistence of both antiferromagnetic and ferroelectric orders, as discussed in Chapter 1. The magnetic and lattice vibrations, as well as their hybridizations, dominate the dynamical properties of these multiferroics.²⁷⁴⁻²⁷⁵ In addition to conventional transport measurements to study the characterizations, as well as theoretical efforts contributing to the better understanding of coupling mechanisms, ultrafast optical spectroscopy is a powerful technique that can resolve dynamics temporally, and thus offers another effective method to study the coupling between multiple degrees of freedoms.

Ultrafast optical spectroscopy is used to study carrier dynamics and couplings between different degrees of freedom on extremely short time scales (nanoseconds to

Figure 6-1 “Schematic layout of the magneto-optic experimental arrangement. The inset is the micrograph of microfabricated coil and sample. PD: photodiode, P1: polarizer, P2: Thompson polarizing beam splitter, BS1: 10% beam splitter, BS2: 50% beam splitter, PR: polarization rotator, DL: delay line, MO: microscope objective, DA: differential amplifier, PC: photoconductive switch, S1: GaAs substrate, S2: SiO₂ substrate, and V: bias voltage.” Figure taken from Ref. [280].

femtoseconds). It has contributed to our understanding of electron-phonon scattering, electron-electron scattering, coherence effects, effects of quantum confinement and electronic transport upon these processes in chemistry, biology and physics.²⁴⁶ Advances in ultrafast optical spectroscopic technology include that the generation and detection of sub-picosecond pulses range from the far-infrared to the visible, and even into the X-ray region of the electromagnetic spectrum. Lim *et al.* discussed the coherent excitations of

acoustic and optical phonons in multiferroic LuMnO_3 .²⁷⁶ Talbayev *et al.* reported that in multiferroic $\text{Ba}_{0.6}\text{Sr}_{1.4}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ a magnetic resonance mode was detected.²⁷⁷ Takahashi *et al.* found an ultrafast modulation of the electric polarization resulting from the injection of charge carriers and the subsequent acceleration.²⁷⁸ Here we suggest a novel ultrafast approach of directly measuring the reversal rate (and hence the ME coupling). This novel approach is modified based on measuring the time-resolved magneto-optic Faraday and Kerr rotation (MOKE = magneto-optic Kerr effect).²⁷⁹ Elezzabi *et al.* measured the spin-lattice relaxation time in Au directly, with the magneto-optic experimental arrangement shown in Figure 6-1.²⁸⁰ The GaAs based Auston Switch was used to optically switch picosecond risetime transient magnetic field, and this instantaneous magnetic field with sufficient magnitude leads to the time-resolved polar Kerr rotation, which could be directly measured.

Based on the above ideas, the schematic setup of our novel approach is illustrated in Figure 6-2, which describes how this can be done in a multiferroic thin film. An initial “pump” pulse closes the “Auston Switch” and hence the circuit, causing a current to flow through the loop and generating an ultrashort magnetic field through the loop. An electric polarization then develops inside the film and induces a birefringence in the film. A later “probe” pulse detects this birefringence using a balanced detector configuration, as a function of time delay between pump and probe. By measuring how fast the magnitude and direction of this electric polarization relaxes in different nanocomposites structures, we can engineer fast switches in magnetoelectric devices.

Figure 6-2 Schematic of a pump-probe setup to measure the ME coupling in a multiferroic thin film.

§ 6.2 Sample Preparation and Characterizations

In the pump-probe experimental setup (see Figure 6-2), a pulsed current is needed in order to generate an ultrashort magnetic field. Thus the photoconductive Auston switch is introduced, which is triggered by an ultrafast optical laser pulse and then generates a current transient in a coplanar wave guide.²⁸¹ Previous work reported the rise time of the pulse is dominated by the carrier mobility and optical pulse width, while the fall time is governed by the carrier lifetime due to recombination and sweep-out in the presence of the bias field.²⁸² That requires the photoconductive Auston switch with ultrashort carrier lifetime for ultrafast switching, high electric breakdown field, high mobility for good optical responsivity and low dark current. Various semiconductors, e.g. amorphous, impurity-dominated and intrinsic, are explored as photoconductive Auston switch.²⁸³⁻²⁸⁵ In particular, low-temperature grown GaAs (LT-GaAs) becomes the ideal candidate in this

ultrafast application due to its good optoelectronic and electrical properties. LT-GaAs is nonstoichiometric arsenic-rich GaAs grown by molecular beam epitaxy (MBE) at 200 °C and annealed at 600 °C.²⁸⁶ Compared with the normal GaAs, LT-GaAs has excess arsenics in the most common forms of gallium vacancies V_{Ga} , arsenic interstitials As_i and arsenic-antisite defects As_{Ga} , which are responsible for high breakdown field and carrier mobility.²⁸⁷

Figure 6-3 (a) I-V curves of LT-GaAs shows Ohmic contact behavior with the applied voltage up to 200 V. (b) The resistance of LT-GaAs remains stable for all applied voltages.

The purchased LT-GaAs sample (Semiconductor Wafer, Taiwan) was examined by a Keithley 4200 semiconductor characterization system (Keithley, USA). Figure 6-3 presents the typical I-V curves at various applied voltages. High resistance can be achieved around $10^8 \Omega\text{m}$ for all applied voltages. The electric breakdown voltage can be

higher than 200 V. This suggested the LT-GaAs is a good candidate for our experiments.

Figure 6-4 (a) High resolution XRD patterns of BFO thin film grown on the STO substrate.

BFO thin films were epitaxially grown by PLD on (001) SrTiO₃ (STO) substrates. The growth parameters are the same as that discussed in Chapter 5. High resolution XRD spectra demonstrate the crystallinity and crystal orientation of BFO thin film, as displayed in Figure 6-4. The position of 002 peak is $\sim 44.43^\circ$, larger than that ($\sim 38.64^\circ$) of the BFO thin film grown on SLAO. The calculated out-of-plane c lattice parameter ($4.07 \text{ \AA}$) is smaller than that on SLAO ($4.66 \text{ \AA}$), but still a little larger than the value of bulk BFO ($3.96 \text{ \AA}$).²⁵⁹ It is ascribed to the lattice mismatch between BFO thin films and substrates. Figure 6-4 shows the topographic and piezoresponse out-of-plane amplitude images of BFO thin film. As shown in Figure 6-5(a), the BFO thin film has a uniform surface containing regular domains, with roughness $R_{\text{rms}} \sim 3.17 \text{ nm}$. The out-of-plane PFM image shows a uniform contrast with all polarizations pointing “up”, as shown in Figure 6-5(b), opposite to the direction for BFO thin films grown on SLAO. This polarization agrees

with that in the previous report.²⁸⁸

Figure 6-5 Topography (a) and out-of-plane PFM (b) images of BFO thin film on STO substrate.

§ 6.3 Device Fabrication and Experimental Setup

Photolithography and Au wire bonding were performed on the device fabrication of LT-GaAs-BFO, according to the schematic shown in Figure 6-6(a). Positive photoresist was deposited on both BFO thin film and LT-GaAs wafer uniformly by spin coating at 9000 rpm for 90 seconds, and then preheated at 110 °C for 4 min. The UV light was shined on the designed photomask whose bottom was attached samples for 40 seconds, transferring the patterns on the surface of samples. Then the developing solution was used to develop those photoresist exposed under UV light. After that, Ohmic-contact electrodes were coated on samples, and connected by Au wire bonding.

Figure 6-6 shows the various components of the Auston Switch device. According to Biot-Savart law, the produced magnetic field is determined by the diameter of the current ring as well as the current. The “finger” structure enlarges the area for the excitation of carriers when the laser pulse hits the fingers, and thus the total current (= carrier density ×

area of the photoconductive Auston Switch) increases. Here Au loops with different diameters, and photoconductive Auston Switch with different “finger” numbers, are fabricated by photolithography, as shown in Figures 6-6(b), (c), (e) and (f). For the pump–probe experiment in reflection geometry ($\Delta R/R$), as illustrated in Figure 6-7, a pump laser pulse was induced to control the photoconductive Auston Switch and a probe laser pulse would detect the corresponding signal.

Figure 6-6 (a) Autocad figure for the designed photomask. (b) and (c) SEM images show Au loops with different dimensions. (d) Photo of entire Auston Switch device. Compare this with Figure 6-6(a), the BFO grown on the substrate at the middle is light yellow, and the loops are fabricated on top of the BFO. The three large dark pieces surrounding the middle square are the Au electrodes deposited on LT-GaAs, where the fingers are located. Contacts were made using wire bonding. (e) “Fingers” of the Auston Switch where the pump pulse hits, (f) Blowup of one finger, showing clearly the gap between the fingers. The dark area is LT-GaAs, while the lighter area is the Au electrodes deposited on top of LT-GaAs.

Figure 6-7 Schematic (a) and photo (b) of the pump-probe experimental setup.

§ 6.4 Dependence of Laser Pump Power and Applied DC Voltage

Figure 6-8 presents the resistance of the circuit versus time. When the pump pulses impinges upon the Auston Switch, the circuit is closed, hence resistance approaches zero. When the pump pulse is blocked, the circuit is open, hence the circuit resistance increases to $\sim 10^9 \Omega$. This preliminary experiment shows that the Auston Switch circuit works, and is sensitive to the presence or absence of the incoming pump pulse.

We performed a simple pump-probe experiment in reflection geometry ($\Delta R/R$), with the setup as shown in Figure 6-7. There is no pump-probe signal observed. That might be due to the weak ME effect in BFO thin film. The current generated in the circuit and its sensitivity to laser are critical in our experiment. Since the sensitivity to the presence or absence of the incoming pump pulse is demonstrated in Figure 6-8, we next examined the dependence of laser pump power and applied voltage to the generated current. The LT-GaAs-BFO device we examined has 7 “fingers” on the Auston Switch, and the

Figure 6-8 Resistance of the circuit in Figure 6-2. When the pump pluses impinges upon the Auston Switch, the circuit is closed, hence resistance approaches zero. When the pump pulse is blocked, the circuit is open, hence the circuit resistance increases to $\sim 10^9 \Omega$.

diameter of Au loop on top of BFO is 40 μm . Different laser pump power were applied with maximum pump power of 18 mW (KM Labs Griffin) at the applied DC voltage of 1 V and 10 V, respectively. The measured currents are compared in Figure 6-9. It indicates that the sensitivity is always good, and the generated current is proportional to laser pump power and applied DC voltage. We chose both maximum values to calculate the generated magnetic field inside the Au loop, and obtained a calculated magnetic field of $\sim 10^{-5} \text{ T}$, which would lead to a much smaller ME effect in the BFO thin film.²⁸⁹

In the future, we will perform the following: Firstly, in order to generate larger current in the circuit, we will use an amplified laser (Coherent RegA, 250 kHz repetition rate) with a 3 orders-of-magnitude higher laser fluence than that of Griffin laser. Secondly, we will perform measurements of time-resolved magneto-optic Faraday and Kerr rotation

with the purpose to investigate the ME coupling induced spin dynamics in BFO thin films.

Figure 6-9 Measured current as a function of laser pump power and applied DC voltage.

§ 6.5 Summary

A novel ultrafast approach is presented here, which seeks to measure the ME coupling by measuring the time-resolved magneto-optic Faraday and Kerr rotation (MOKE = magneto-optic Kerr effect). Based on this approach, LT-GaAs-BFO device is characterized, and fabricated by photolithography and Au wire bonding. Preliminary results show that the device is sensitive to the presence or absence of the incoming pump pulse. The measured current increases with increasing laser pump power and applied DC voltage. We did not see any pump–probe signal from the simple pump–probe experiment in reflection geometry ($\Delta R/R$). Next, we will take the measurement of time-resolved magneto-optic Faraday and Kerr rotation by using an amplified laser.

Chapter 7 Conclusions and Future Works

§ 7.1 Conclusions

In conclusion, this dissertation is mainly focused on the synthesis and characterization of epitaxial nanocomposites of strongly-correlated electron systems, which particularly refer to transition metal oxide of ZnO and multiferroic BFO materials. The interplays among the spin, charge and orbital degrees of freedom introduce novel physical properties including room temperature ferromagnetism and multiferroic functionalities. Besides the traditional characterization techniques, THz-TDS offers an advanced technique to investigate the complex conductivity and dielectric response in THz spectral regime uniquely, with its energy on the same order of that in the strongly-correlated electron systems.

ZnO is one of the most vital and versatile functional metal oxides in various forms including ceramics, thin films and nanostructures. The electrical, magnetic and optical properties can be modified by the effect of doping. In order to unravel the mechanisms in this material system, we systemically investigated the doping effect in Ag- and Cu-doped ZnO bulk ceramic samples. Mott and Efros VRH were employed to explain the temperature dependent resistivity. The percolation-based model of partially ordered BMPs plays a pivotal role to the presence of room temperature ferromagnetism. Hall Effect results suggest carriers in Ag- and Cu-doped ZnO bulk samples are localized, whereas a semiempirical model can well describe the temperature dependent MR, which combines both positive and negative contributions of magnetoresistance.

Using these Ag- and Cu-doped ZnO bulk samples as the PLD targets, we synthesized Ag- and Cu-doped ZnO thin films on the z-cut quartz. Z-cut quartz shows a THz frequency independent refractive index with a small absorption coefficient, indicating a good choice of substrate used in THz-TDS. Almost no absorption of THz pulse for Cu-doped ZnO thin film suggested its high insulating property. The measured complex conductivities of undoped and Ag-doped ZnO thin films are well described by the Drude-Smith model. As temperature increases, the extracted carrier density increases but relaxation time decreases for the undoped ZnO thin film, while that for the Ag-doped ZnO thin film has no obvious dependence of temperature. These results suggesting our samples are in the localized regime.

To achieve rich functionality, multiferroics has been another interesting research area which promises potential applications in multifunctional devices. As the substrate used to grow BFO thin films, SLAO single crystal was characterized by THz-TDS firstly. The complex dielectric responses are well fitted by Drude-Lorentz model with two resonance modes. Thermal annealing leads a great reduction of free charge carriers in the substrate, removing the Drude contribution, leaving only the Lorentz term. By using the extracted refractive index and absorption coefficient of SLAO, we investigated the THz response of BFO thin film grown on the two-side polished SLAO substrate, using the annealed SLAO as a reference.

Further, a novel ultrafast approach is presented which seeks to directly measuring the reversal rate (and hence the magnetoelectric coupling) by measuring the time-resolved magneto-optic Faraday and Kerr rotation. Based on this approach, LT-GaAs-BFO device is characterized, and fabricated by photolithography and Au wire bonding. Preliminary

results show that the device is sensitive to the presence or absence of the incoming pump pulse. The measured current increases with increasing laser pump power and applied DC voltage. We did not see any pump–probe signal from the simple pump–probe experiment in reflection geometry ($\Delta R/R$). Next, we will take the measurement of time-resolved magneto-optic Faraday and Kerr rotation by using an amplified laser.

In summary, we have synthesized Ag- and Cu-doped ZnO samples in the morphology of bulk ceramics and thin films, and various characterizations were applied to study their electrical, magnetic and THz properties, with the purpose of unraveling the various cross couplings in strongly-correlated electron systems. Moreover, multiferroic BFO thin films grown on the SLAO substrate was investigated by THz–TDS. Besides, a novel ultrafast approach is presented which seeks to directly measuring the reversal rate (and hence the magnetoelectric coupling in BFO thin films) by measuring the time-resolved magneto-optic Faraday and Kerr rotation. Such basic but vital studies help us to address the cross coupling among charge, spin and orbital degrees, and give insight to the future either for the fundamental physics or for the potential applications.

§ 7.2 Future Works

To continue this work, the interplays between the orders of freedom (spin, charge and lattice) as well as their couplings will be investigated by ultrafast optical spectroscopy, with the purpose of unraveling the origins of various functionalities and shedding light on the potential applications. BFO is one of the most actively studied multiferroic materials as it possesses ferroelectric and magnetic orders simultaneously at room temperature. Epitaxial BFO based nanocomposites offer a very exciting opportunity to study the

competition or collaboration between different orders of freedom.

ME effect in BFO has created great interest in recent years, but the origin is still debated. Ultrafast optical spectroscopy has been employed to study magnetic and lattice excitations which are responsible to the observed ferroelectricity and magnetism.^{41-42,251} Far-infrared spectroscopic studies on multiferroic manganites suggested the magnons were mixed with phonons in microscopic ME interactions.²⁹⁰⁻²⁹¹ THz spectroscopic studies on bulk BFO demonstrated the electromagnon excitation resulting from the ME coupling, and the anisotropy of observed resonance modes were dominated by the magnetic-dipole selection rule.⁴² In the Chapter 5, we performed the THz response of the BFO thin film grown on SLAO by using THz-TDS. Since the film thickness was small, which led a small difference between the THz signals of the film sample and SLAO reference, we will investigate the THz response of thicker BFO thin films to study the ME coupling mechanism.

Besides the THz spectroscopic study of the magnetic and lattice excitations in BFO thin films, a novel ultrafast approach was employed by measuring the time-resolved magneto-optic Faraday and Kerr rotation (MOKE = magneto-optic Kerr effect), as described in Chapter 6. Preliminary results showed the fabricated LT-GaAs-BFO device is sensitive to the presence or absence of the pump laser. So far we performed the simple pump-probe experiment in reflection geometry ($\Delta R/R$), but did not detect the signal. Further, we will employ an amplified laser (Coherent RegA, 250 kHz repetition rate), which has a 3 orders-of-magnitude higher laser fluence than that of Griffin laser, to generate larger current. Also, we will perform time-resolved magneto-optic Faraday and Kerr rotation measurements on the LT-GaAs-BFO device. This novel approach offers an

unique opportunity to study the ME effect directly, and hopefully can be applied to other material systems, giving insight on the dynamics of different orders.

The entanglement of the spin, charge and orbital degrees of freedom gives rise to various phenomena, and thus has drawn a burst of activity in manipulating these phenomena, especially in the systems with the oxide interface.²⁹² There are three important symmetries: broken spatial inversion (I) symmetry can lead to spontaneous electric polarization, broken time-reversal (T) symmetry is associated with the spin operator, and broken gauge (G) symmetry corresponds to superconductivity or superfluidity.²⁹³ The various symmetry-breaking patterns offer novel emergent phenomena.²⁹⁴⁻²⁹⁵ BFO is a good candidate because of the unique ferroelectric and magnetic properties, while YBCO is a typical high-temperature superconductor. The interface between BFO and YBCO epitaxial thin films leads to symmetry breaking, and some novel behaviors emerge. Researchers have paid great attention on the studies of this ferroelectric/superconducting heterostructures system.^{38,296-299} Here we will perform the THz response of the BFO-YBCO thin film grown on the $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) substrate, by comparing with that of the YBCO and BFO thin film, in order to underline the mechanism of the interface effect. Such a study helps us well understand the interface effect, offer us an opportunity to manipulate or even design new heterostructures with valued functionalities.

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